REFINER
AND NATURAL GASOLINE MANUFACTURER

AUGUST, 1939
Vol. 18, No. 8

A Gulf Publishing Company Publication
EDITED MONTHLY AT HOUSTON, TEXAS

Copyright, 1939

GRADY TRIPLETT
Editor

CONTENTS

Application of Automatic Controls 57
A. J. Foley

Modern Instrumentation for Topping, Cracking and Polymerization Plants 60
Donal J. Bergman

Melting Point of Solid Greases 68
D. S. Velikovskii, I. P. Lukashevich and F. L. Borshchevskaya

Steam at Low Cost in Wilshire Power Plant 74
J. C. Albright

Experimental Studies in Non-Fluid Lubrication (Part 2) 76
S. Kyropoulos

Helium—Its Sources, Production and Use 81
A. W. Trusty

Modernized Cracking Plant Has Novel Features 83

Economics of Catalytic Polymerization of Natural Butanes 86
F. B. Mack

Hydrogen Sulfide Removal 90
H. N. LaCroix and L. J. Coulthurst

Departments

The Look Box ..... 53 and 101

Too Much Gasoline on Hand 55
L. J. Logan

Plant Activities 114

Science and Technology (Abstracts) 120

New Equipment for the Modern Plant 130

Business Notes 136

Catalogs and Bulletins 140

Ideas to Help Plant Efficiency 96

Advertisers' Index 142

SPECIALIZED OIL JOURNALS

Published by

THE GULF PUBLISHING COMPANY

OFFICE OF PUBLICATION
3301 Buffalo Drive, Houston, Texas

R. L. DUDLEY, *President*
A. L. BURNS, *General Manager*
S. W. ROBINSON, *Editorial Director*
J. KENT RIDLEY, *Managing Editor*

NEW YORK: Room 625, 250 Park Avenue, Dick Swinsky, Manager.

PITTSBURGH: 72 Vandergrift Building, Chas. A. Wardley, Manager.

CHICAGO: 332 S. Michigan Avenue, H. G. Fitzpatrick, Manager.

LOS ANGELES: 425 W. W. Wilson Building, Huntington Park, California, Jay Curts, Jr., Manager.

TULSA: 1513 Hunt Building, J. F. Carter, Jr., Manager.

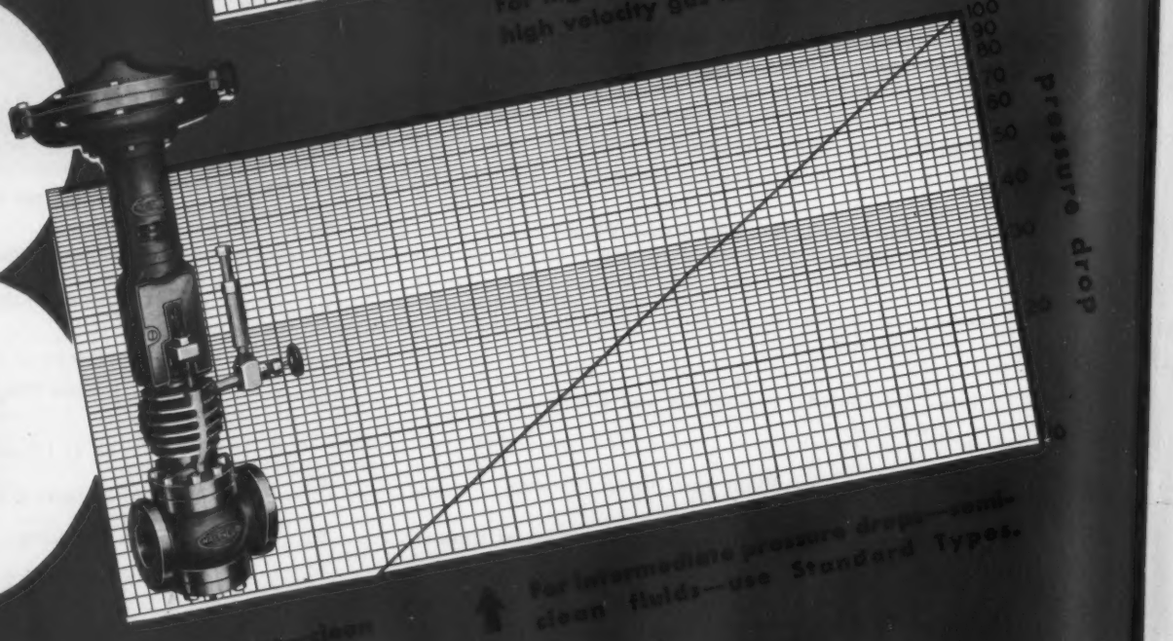
FT. WORTH: 203 W. T. Waggoner Building. H. H. King, Manager.

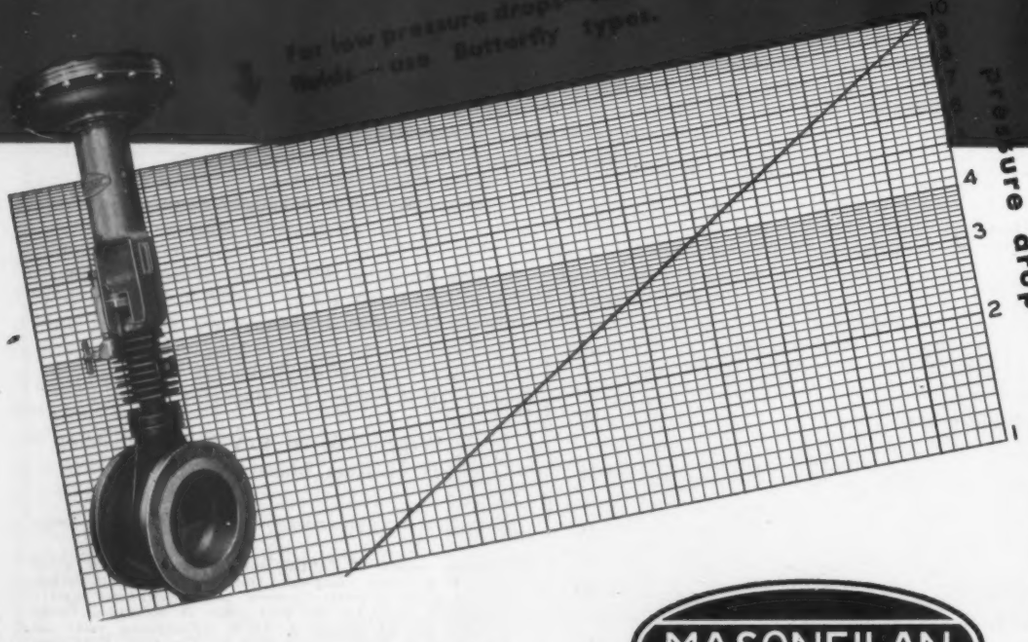
Single copies 20 cents. Domestic subscription price $1.00 a year. Canada and Foreign subscription price $2.00 a year. Entered as second class matter June 16, 1923, at the post office at Houston, Texas under act of March 3, 1879. Advertising rates on application.

Copyrighted 1939 by The Gulf Publihing Ccmpany.

IN ANY REFINERY THESE ARE THE . .

BIG 3





THESE three outstanding contr valves cover the full range of au matic control requirements—fr transfer line back pressure, char or "resid" and bottom draw-off, cooling tower water service; fr high pressure, high temperature low pressure, low temperature s vice; from hot oil and coke to cl liquids. In short this line offers correct valve for any given refin process. Each is unique in desi —developed by Masoneilan gineers. Any of them may equipped with the distinct Masoneilan manual operating u and multiplying position indicato

Specify Masoneilan Control Valv —the valves engineered to me *your* requirements.

MASONEILAN
REG. U.S. PAT. OFF.

1182 ADAMS STREET
BOSTON, MASS., U. S. A.

NEW YORK BUFFALO
PHILADELPHIA PITTSBURGH CHICAGO ST. LOUIS TULSA HOUSTON LOS ANGELES

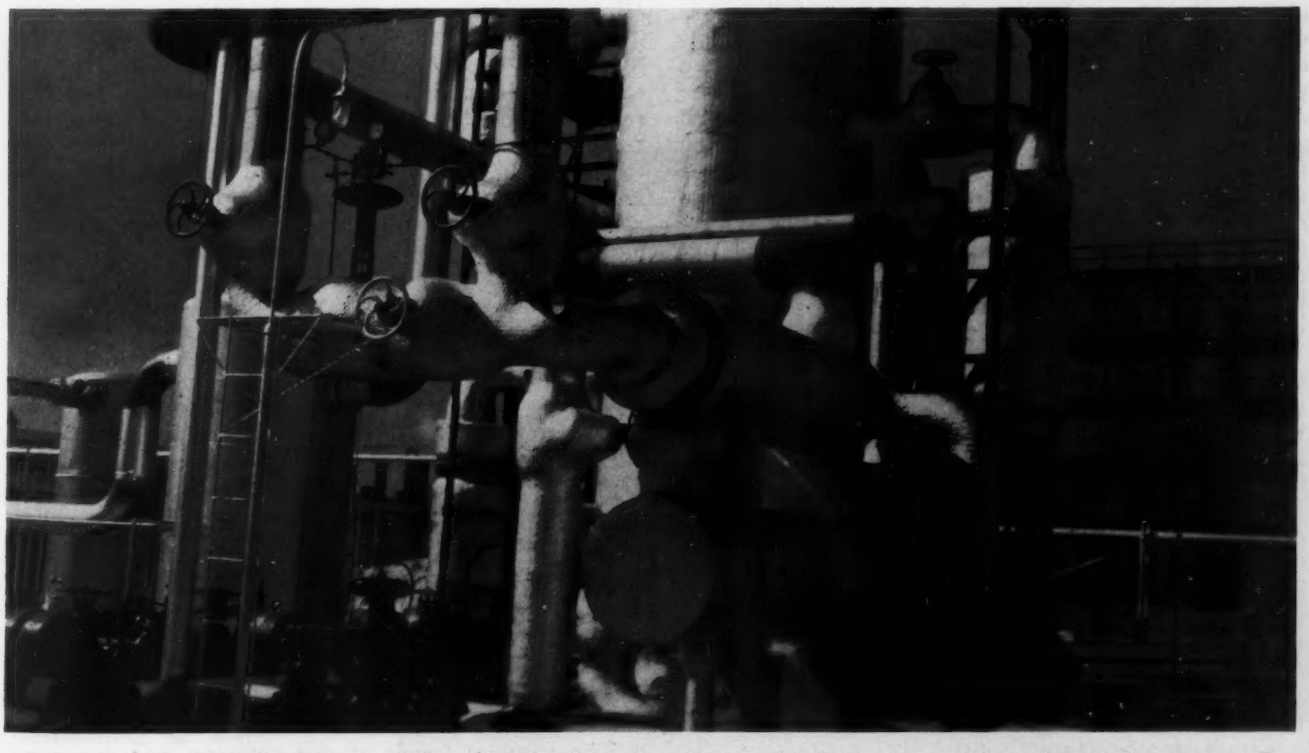
Application of Automatic Controls

A. J. FOLEY
Hanlon-Waters, Inc.

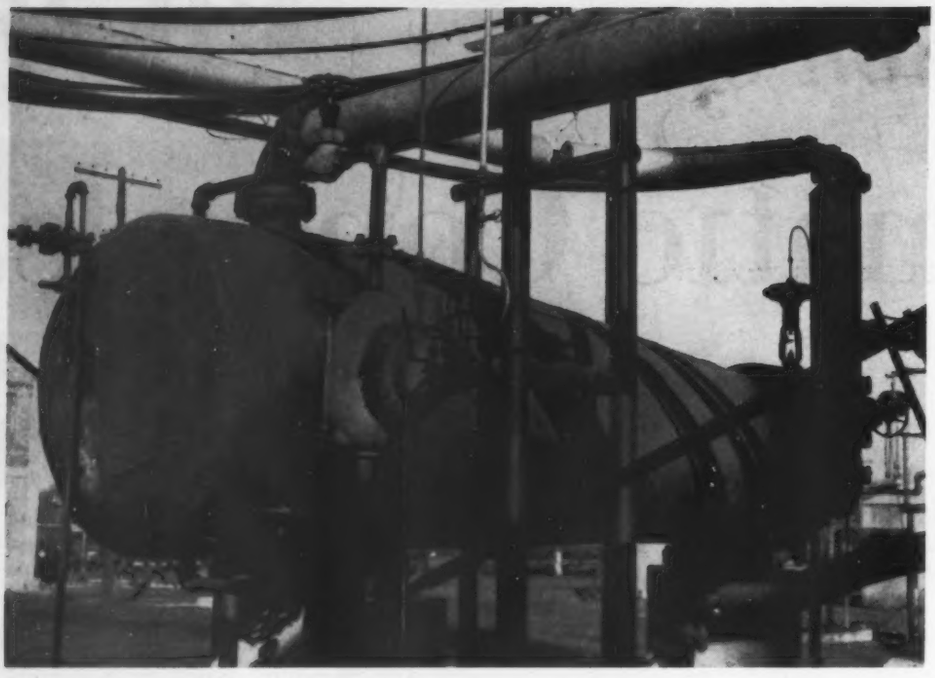
IN this discussion the application of automatic controls is treated in the broad sense, including not only the selection of the most suitable device for the the purpose, but other factors that influence a successful application, such as proper installation, adjustment and maintenance.

M. F. Behar in his "Fundamentals of Instrumentation" states, "From the viewpoint of the industrial engineer, the application of an instrument is of far greater importance than the instrument itself. Proper installation counts more than intrinsic accuracy. The usefulness of instruments depends on proper appreciation of their uses." One automatic control manufacturer cleverly drew an analogy to this by depicting a pair of hands with boxing gloves attempting to operate a typewriter, pointing out that the gloves and the machine were the best that money could buy but the operation failed as both articles were not being used for the purpose for which they were designed.

Any instrument or control no matter how well designed, or carefully manufactured, will fail if improperly applied or installed. Each device has its limitations beyond which it is useless. The competent automatic control sales engineer is cognizant of the limitations of each device he handles as well as its advantages. He, therefore, avoids recommending devices for improper applications, resulting in savings to the prospective user of time, money and material. If costly misapplications are to be avoided it is necessary for the user to give the manufacturer the closest cooperation by supplying all operating conditions, results desired, and relationship of the proposed control to other controls in the process. This last frequently requires a careful study of the process flow charts. The buyers who give the manufacturer the most assistance along these lines are the ones who have the least difficulties with their controls. Automatic regulation is a highly specialized science and buyers can profit from the suggestions



Control valves in gasoline plant used to control flow of refrigerating medium through a special absorber used to obtain greater recovery of low boiling fractions.



Liquid level controller controlling liquid from reboiler in stabilizer system and cracking plant.

offered by the engineers engaged in this specialized profession.

The following examples illustrate the importance of proper application and are drawn from actual installations made during the past.

Some time ago a large crude-distillation pipe still unit was built for a Mid-Western refinery. At that time the art of refining and instrumentation had not reached their present high state of perfection as for example, rate-of-flow controllers were not yet available. The unit was complete, producing cracked gasoline, straight-run gasoline, kerosene, V.M. & P. naphtha, light wax distillate, heavy wax distillate, gas oil and fuel oil. It was equipped with four fractionating towers and the furnace was provided with two passes, each having a set of charge pumps. The crude after leaving the crude pumps passed through several vapor-heat exchangers in series, and then through reflux condensers on the top of each bubble tower in series. The crude then entered the bottom of the first tower and the bottoms of this tower were picked up by the first-pass charge pump and put through the first pass of the still. A liquid-level controller on the bottom of this tower controlled the incoming crude as the first-pass charge would vary. The temperatures of the vapors leaving all four towers were controlled by thermocouples placed in the vapor lines and through potentiometers, actuated motorized valves in by-passes in the crude lines around the reflux condensers. As the vapor temperatures increased the motorized valve would close to force more crude through the reflux condenser, thereby cooling the vapors. This arrangement seemed feasible on paper, but the temperature controllers had the disadvantage that the crude temperature would vary as the performance of the preceding controller varied. When the liquid level in the bottom of the first tower built up, closing the level control valve in the crude inlet, the circulation in all the reflux condensers would stop and render all the top-tower-temperature controllers ineffective. To remedy this, it would be necessary to rearrange all the controllers and redesign the flow chart of the unit.

The temperature of the oil leaving each pass of the still was controlled by thermocouples placed in the transfer lines and through potentiometers, actuated motorized valves in the steam lines to each charge pump to vary the throughput with variations in the transfer temperature. Then, as the transfer temperature increased, the charge pumps would speed up to keep the temperature normal. This was to be accomplished with a constant firing rate to the furnace. This control arrangement did not function at all, as the large time lag of the oil from the pump discharge to the transfer line prevented the controller from reaching equilibrium.

On the absorption vapor-recovery plant of another refiner, difficulty was being experienced with the temperature controller on the bottom of the still. At times this temperature would rise suddenly and later quickly fall. The instrument, the controlled valve and the installation were carefully examined and checked several times with no avail. The trouble was located in the liquid-level controller on the bottom of the absorber, which throttled the flow of rich oil to the still. This level controller was sticking so that it was producing on and off instead of throttling control. These sudden changes from no flow to full flow were causing the sudden temperature variations in the bottom of the still. The level controller being of the direct mechanically-operated type, it was necessary to carefully adjust and align the levers, turnbuckle, and rods, to remove the bind and secure smooth throttling control. After doing this the temperature at the bottom of the still settled down and remained uniform. To secure the best performance from these direct mechanically-operated liquid-level controllers, it is advisable to give a few turns to the grease cartridge lubricators on the stuffing boxes and apply a few drops of oil to the clevice pins, thereby obtaining smoother action.

The vacuum tower at one refinery was equipped with a pilot-operated liquid-level controller to con-

trol the bottoms outflow. The controlled valve was installed in the bottoms-pump discharge line. At times the tower would go dry and the pump would lose suction. An examination of the level controller disclosed that it was in good working order. The trouble was caused by the controlled valve being too small, and the operators opening the by-pass around it. Then, at low rates the controlled valve would be closed but the tower would be pumped dry through the by-pass.

On a newly-constructed refining unit the liquid-level controller on the distillate receiver was apparently doing its duty for several days. Later, difficulty was encountered in maintaining the receiver level. This was due to the stop valves on the float cage equalizing lines not being opened when putting the unit on stream, thereby preventing the level controller from operating.

A refiner had gas at 200 pounds in a vessel and wished to feed some of this through a pressure-reducing regulator to another vessel some distance away at 100 pounds. Inasmuch as the pressure drop was 100 pounds it was decided to take half this drop through the regulator and the other half through the adjacent piping, so smaller and cheaper piping could be used. The installation did not work well as the regulator gave poor regulation. Since the pressure drop in the piping varies as the square of the velocity, variations in flow rates changes the piping drop considerably and prevents good regulation. In this case the piping was similar to an elongated orifice, having as much control over the pressure as the regulator. In order for a regulator to function properly it must dominate the situation by having the major pressure drop across it and only a minor pressure drop in the adjacent piping.

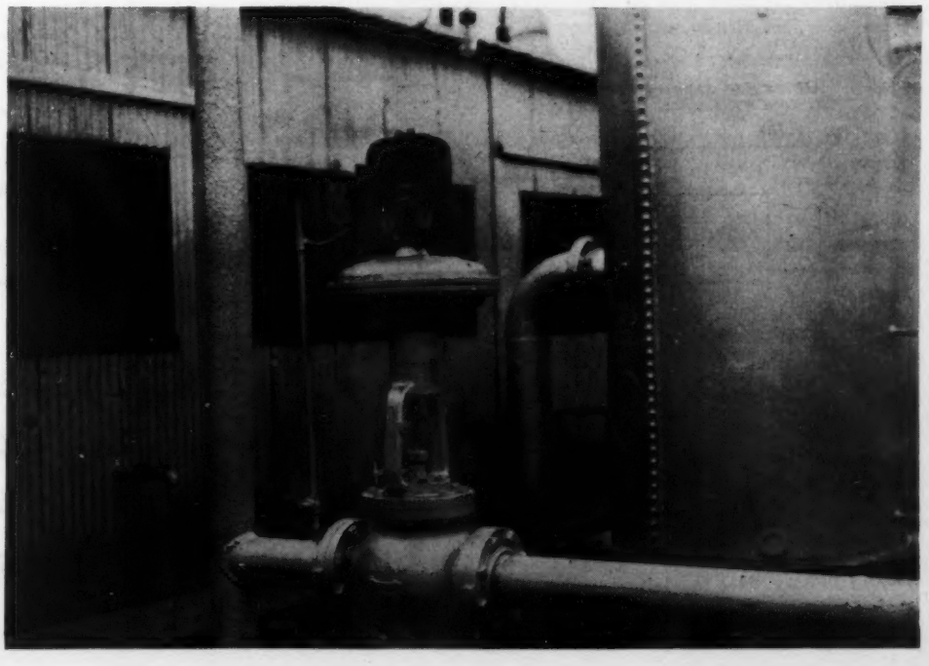
The temperature controller on a pressure-distillate stabilizer-reboiler operated satisfactorily for several days after installation, and then the temperature gradually fell off without coming back. Nothing could be found out of order with the instrument or controlled valve on the steam supply. The by-pass was opened but did not bring back the temperature. The steam trap draining the reboiler coil was operating properly. The unit was then shut down and the steam tubes cleaned. After starting operation again, the temperature remained at the control point for several days and then again fell off. The trouble in this case was due to the reboiler being too small for the job, not having enough heating surface, and the small difference between clean, and slightly dirty tubes prevented satisfactory operation.

The pilot operated back-pressure regulator holding the back pressure on a gas absorber would not hold the pressure at the set point, allowing it to fall off. All adjustments of the regulator were checked without results. The difficulty was caused by a piece of coke wedged under the reverse-acting inner valve, preventing it from closing.

The improper sizing of regulators has been the cause of many troublesome installations. In some cases this has been due to the buyers not supplying sufficient operating data to the manufacturer. Some has been due to using capacity tables based on arbitrarily assumed velocities which are supposed to remain the same regardless of the pressure drop across the regulator. A regulator can be considered similar to an area-type meter, as the pressure drop is fixed and the orifice size varies with the flow. In an orifice meter the orifice is fixed and the pressure drop across it varies with the flow.

Present day complex processes are analogous to the intricate human system and modern instrumentation working on trouble jobs is similar to the physician diagnosing a patient's illness. The trouble displays certain symptoms that may be due to a number of causes. By a process of testing, checking and elimination the instrumentation locates and rectifies the trouble whether it be in the controller, adjustment, installation or in the process.

If the foregoing general comments will serve to focus more attention to the proper application and installation of automatic controls, they will have served their purpose.



Pressure controller in gasoline plant regulating pressure of gas leaving plant for use in repressuring in nearby oil field.

Modern Instrumentation

for Topping, Cracking, and Polymerization Plants

DONALD J. BERGMAN
Chief Engineer, Universal Oil Products Company

THE strides in mechanization and production which have resulted in the present high ratio of automobiles to population in the United States have been paralleled by advances in the oil refining industry. It is only a few years since a sparkling clear straight-run gasoline with an octane rating of perhaps 45 or 50 and an Engler endpoint of 425° F. was considered to be the ideal fuel for the motor industry.

Since then, first thermal cracking and reforming, and more recently polymerization and catalytic cracking have held the spotlight as the means for producing motor fuel of the desired characteristics.

Whatever the means employed, the necessity of obtaining maximum yield and maintaining uniformity of product has resulted in the rapid development of control instruments to replace the older methods of hand control. The modern large combination topping and cracking unit has become so complex and has so many instruments indicating or recording and controlling temperature, pressure, flow and liquid level, that there would hardly be floor space in front of an instrument board for the number of operators required, if all these points had to be controlled by hand.

In the past, control instrumentation on oil refining processes has arisen out of the direct replacement of an indicator or recorder and hand control of some function, by a corresponding automatic controller. An illustration is the replacement of hand control of flow or reflux to the top of a fractionating column by an automatic temperature controller.

In this instance, the mechanism of control is changed in the transition from hand to automatic control. Under hand control the operator set a valve in the steam line to a pump, or a throttling valve in

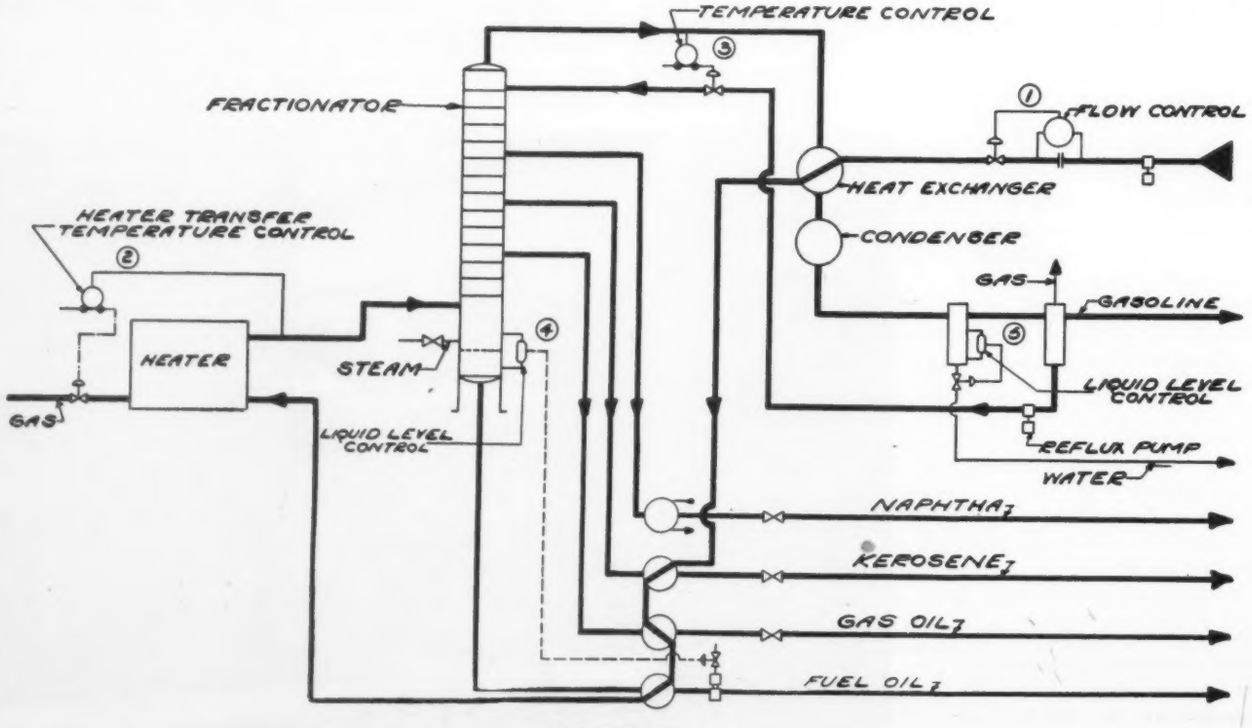


FIGURE 1
Schematic Flow Diagram of Crude-Topping Unit.

the reflux line to the tower, if the pump was provided with a pressure governor. Or perhaps he changed slightly the orifice in the pump speed regulator, if that was still in working order. At any rate, he made an endeavor to fix a constant flow which would hold until the temperature at the top of the column deviated far enough from the desired point to call his attention and he found it necessary to make another change.

The first automatic controllers supplied for this duty usually functioned to increase the flow of reflux when the temperature went up and decrease the flow when the temperature went down, and this they would continue to do, often very much like a heavy handed new operator who was not only too quick to make a change, but also made too much of a change each time. As a result, automatic temperature control of a tower top often resulted in a continued zigzag line between narrow or wide limits, depending upon the load on the tower, the characteristics of the instrument, size of control valve, and the provision of by-passes, air capacity tanks, etc., so that the operator could more or less approximate the original condition of uniform flow.

Within the past few years there has been a consistent effort by instrument manufacturers and engineers to arrive at a more logical method for obtaining the desired characteristics in the control instrument based upon certain physical constants in the process, and in the instrument itself.

MATHEMATICS OF CONTROL PROBLEMS

Similar control problems have been encountered in the past in other industries, such as boiler-feed control, turbine regulation, electrical controls, etc., and have been solved by a combination of empirical methods and mathematical analysis. Although the mathematics of control problems has been well recognized in the electrical industry for years, it is only recently that this viewpoint has gained ground in the oil industry. Several articles recently published on the subject should be thoroughly digested by any one having to do with control problems in the oil industry.[1, 2, 3] These articles, while highly mathematical, point out a logical method of attack on the characteristics of a process and the possible influence or interference between the self-regulation of a process and a controller operating on the process. A clearer understanding of the effects of storage capacity for volume or heat in a process can also be obtained by a careful study of the examples given in the articles.

The subject of this paper is too broad to allow of much detailed study of any single process since the ramifications of a given topping or combination topping and cracking plant, as far as effect the control problems, might easily cover much more time than allowed in such a paper. However, it is entirely practical to consider these processes in simplified form from the standpoint of establishing fundamental desirable characteristics.

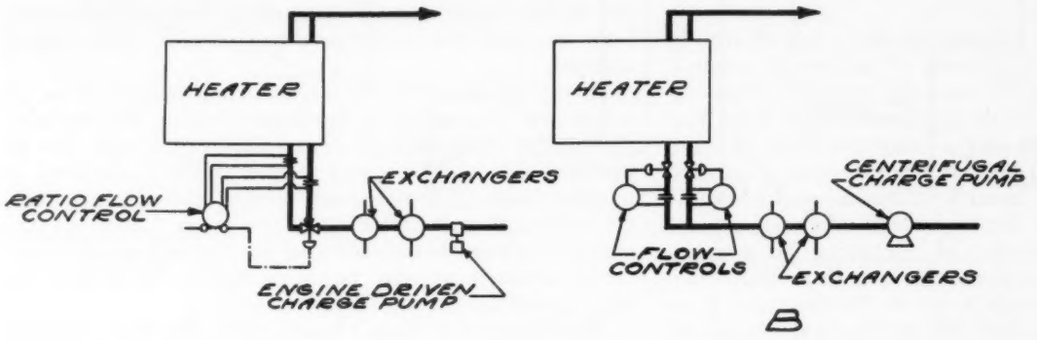


FIGURE 2
Control of Flow to Heater

One feature highly desirable in the majority of processes, and particularly in the processes covered by this paper, is stability or smoothness of operation. In the instrumentation of a plant this should be kept foremost in mind, and where alternate control methods are available for a given point greater weight should be given to the one which tends to smooth the operation as a whole.

PROCESS STABILITY

As a rule, flow control of feed is one of the major factors in obtaining process stability.

The heater is usually the most sluggish piece of equipment as far as responding to changes, therefore it is of advantage to fix its conditions and take up variations at other points. Setting a flow controller on the feed of oil fixes the furnace load. Temperature control on the heater outlet is desirable for maximum stability, because variations in the rate of firing are continued through the rest of the plant.

In the crude topping unit shown schematically in Figure 1, constant control of feed to the unit is almost a basic factor. This should be extended further in the case of a heater with two or more parallel flows. In this case there is liable to be a continuous swing or switching of transfer temperatures of the parallel flows, caused by the variations in friction drop in the region of vapor generation. This is particularly true where the total pressure drop through the coil is small, and variations due to change of

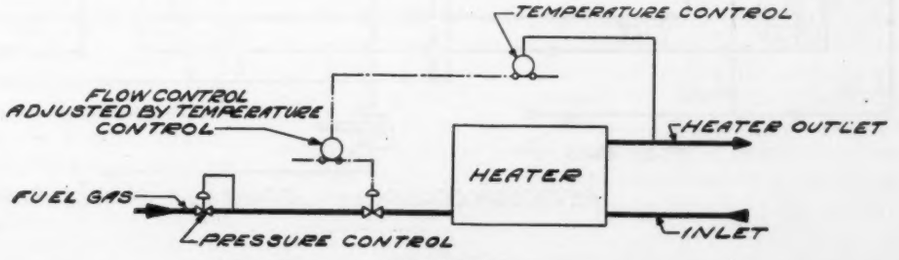


FIGURE 3
Heater Temperature Control Adjusting Flow Control.

state represent a large percentage of the total drop. Figure 2 shows typical hookups of a parallel flow heater to take care of this situation. In case A, an engine-driven reciprocating pump, feeds the crude through the heat exchangers, and the split at the furnace is made by means of a ratio flow controller and a three-way valve. In case B, the charge pump is a centrifugal, and individual flow controllers are provided on each flow.

In Figure 1 the flow control on the crude charge is indicated at (1). The next point of automatic control in the process is the heater transfer temperature controller (2). Together with the flow control to the heater this control provides a constant flow of heat as well as of material to the fractionator. Figure 3 shows a hookup often used in connection with temperature control on a heater outlet where the temperature controller, instead of operating on a valve in the gas to the burners, readjusts a flow controller which operates the master valve to the burners. It is of course presupposed that the gas is under uniform pressure control in either case as fluctuations in gas pressure would make it almost impossible for a controller to keep up with these variations and perform its own duty. The flow controller on the gas is of advantage in maintaining steady conditions in the heater when the operator finds it necessary to readjust individual burners, since even though one or more burners may be put out the predetermined quantity of fuel is continually fed into the firebox. Changes in specific gravity and heating value of the gas are a serious factor in control and these are partially compensated by the use of the flow controller in the gas line.

For control of the gasoline quality from the top of the tower, temperature controller (3) is provided with a valve in the line from reflux receiver to the top bubble tray. This type of installation is typical for a centrifugal reflux pump and is usually preferred for a reciprocating pump with pressure governor, although with proper controller and valve characteristics the installation may be made with a valve in the steam line to the pump. A liquid-level controller (4) at the bottom of the tower controls the rate of drawoff of fuel oil to the heat exchanger. An interface liquid-level controller (5) withdraws water from the water separator. The various cuts of naphtha, kerosene and gas oil are shown as being under hand control.

In this system, on the basis of a constant flow of crude and a constant temperature outlet, the remainder of the controllers have a relatively simple job to perform. The top tower-temperature controller is usually provided with adjustable throttling range and reset, since wandering of the control point is unsatisfactory and the off-and-on action which may result from a narrow band controller is frequently even more unsatisfactory.

With regard to liquid level controller (4), wandering of the control point has almost no significance. Storage volume provided in the bottom of the column can be utilized by a wide throttling range controller of the instrument type, or a ball-float controller with a long arm to give a wide range of travel.

In the same way with the interface level control (5), it is more important to have sufficient sensitivity to detect changes in level than to keep the level exactly constant.

Provision of controls as indicated on the above setup will definitely improve quality of products and through inherent stability will reduce the attention required on the part of the operator to maintain satisfactory control of the plant. Considering for a moment other possibilities, a hand-controlled flow from a centrifugal pump through a heater with hand firing may result in a continual variation of feed and trans-

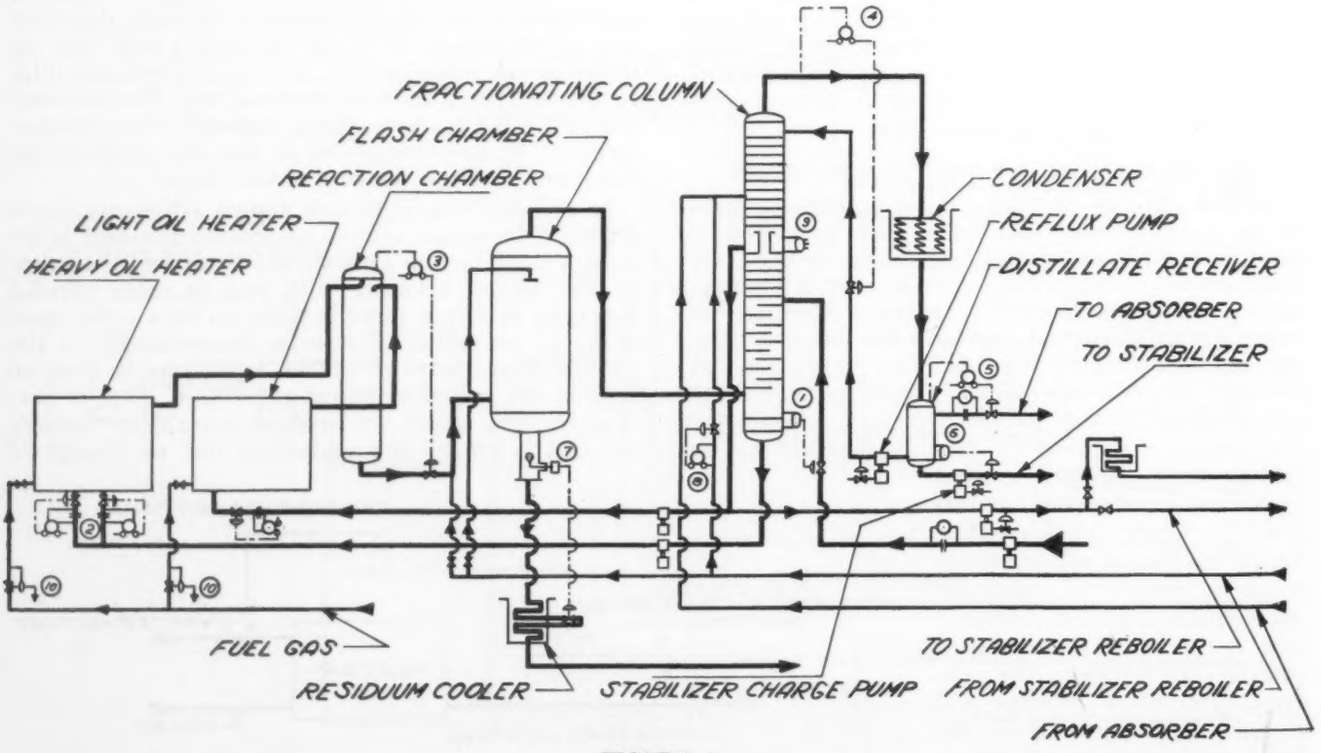


FIGURE 4

Simplified Flow Sheet of Dubbs Selective Cracking Unit, Showing Controls.

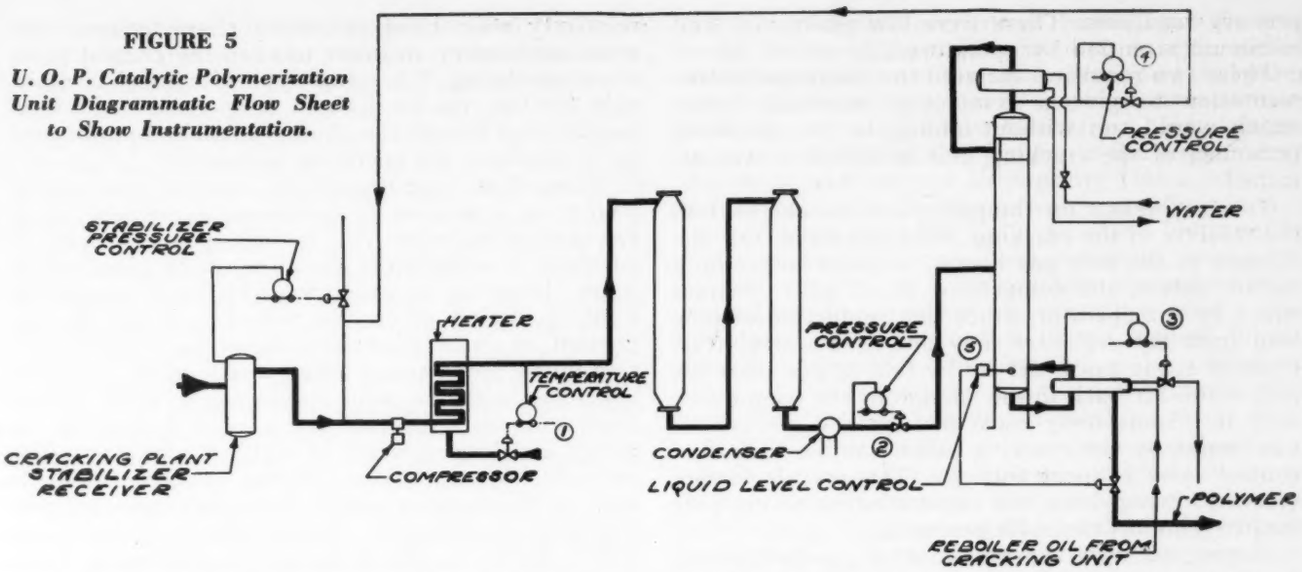


FIGURE 5

U. O. P. Catalytic Polymerization Unit Diagrammatic Flow Sheet to Show Instrumentation.

fer temperature with consequent see-sawing of all the remainder of the controls on the plant.

CONTROL OF CRACKING UNIT

The control system of a modern large cracking unit is even more complicated than that of a topping unit, and in many cases the two are joined together, and their control systems are so intimately related that it is imperative to eliminate the possibility of hunting. In such cases it is often desirable to set up a storage volume between the two systems, and start off the cracking unit with a newly stabilized system, rather than trust to a continuously linked automatic system which may transmit or even amplify any variations or surges.

The many additions possible to a simple thermal cracking plant, such as multiple cracking coils, addition of flashing equipment, gas fractionating towers, control of side streams, stabilization, etc., can result in a system too complicated for analysis as a whole.

Figure 4 shows a simplified Dubbs two-coil cracking unit with the minimum number of controls for satisfactory and smooth operation.

In this case again the heart of the control system is fixed flow to the heaters and flow controllers (2) are provided. Control of transfer temperature is obtained by remote hand control using pressure-balanced valves (10) in the gas lines to each heater. A pressure-balanced valve performs the function of maintaining constant pressure in the burner header as set from the control board. With uniform flow through the heaters this method of operation is quite successful. However, temperature controllers are frequently added in order to obtain the ultimate in control, especially where there is a variation in the quality of fuel gas.

The hot oil from the heaters passes through the reaction chamber and out the bottom connection through a pressure-control valve, maintaining constant pressure on the chamber. With constant flow and temperature through the heaters the duty of this controller is simplified, and since the load is practically constant a wide band proportional controller will do an excellent job. The diaphragm valve on this controller is subject to extremely severe service because of corrosion and erosion. Streamlining the inner body of the valve and the use of special alloy or stellite trim has resulted in a considerable improvement and also a reduction of the possibilities of coking. In the bottom of the flash chamber, liquid level controller (7) releases the residuum through a cooler coil to storage. On account of the possibility of coking this service is rather difficult and attention must be given to cutting down this possibility by introduction of cooling oil at level lines for instrument-type controllers, or at the stuffing box of a float-ball type. Installation of the valve part way through the residuum coil has been found to have advantages over location in the hot section of the line ahead of the cooler or in the cold section after the cooler where sticking may occur.

The top tower-temperature controller (4) is indicated as operating a valve in the reflux line to the top of the tower from a pump provided with a pressure governor. The distillate receiver gas is released by pressure controller (5) and measured by flow meter (11). The distillate product is released from the receiver by liquid-level controller (6). Since in practically all instances a stabilizer is added to the cracking plant for elimination of light ends and meeting specification vapor pressures, a pump provided with a pressure governor takes suction from the receiver and pumps through the liquid level control valve. The charge to the unit passes through flow meter (12) and thence through the valve of a liquid level controller installed in the base of the fractionating column. In this way the feed can be furnished to the column as necessary to maintain a fairly uniform level with a constant charge of combined feed to the two heaters.

These two liquid-level controllers should both be of either wide or extreme band throttling characteristics so that flows will be disturbed an absolute minimum and fluctuations are taken up in the storage space instead of being passed on to other controls. In many cases the flow from distillate receiver to stabilizer is set by a flow controller. In this case, sufficient storage is provided in the receiver so that the operator can watch and make adjustment as necessary, if the level tends to work up or down. A more detailed study of the control problems of a cracking plant has been covered in more detail in an earlier paper.[4]

In the case of the small U.O.P. Catalytic Polymerization Unit, illustrated in Figure 5, there were two

primary requisites. These were low plant cost, and minimum attention by operators.

These two requisites dictated the minimum instrumentation to give a completely automatic plant which would run without adding to the operating personnel of the cracking unit to which it was attached.

The compressor for the poly plant draws gas from the receiver of the cracking plant stabilizer, and discharges to the poly gas heater. In order to set up a stable system, the compressor is set at a constant speed by the operator. Since the production of poly feed from the stabilizer may not be uniform, a recycle of spent gas is set up by taking gas from the poly stabilizer back to the suction of the compressor with the connections made in such a way that the gas vented by the cracking plant stabilizer pressure control valve is spent poly gas. This recycle further serves to bring down the olefin content of the poly feed to the most desirable percentage.

Having set up a constant feed of gas to the poly heater, an automatic temperature controller (1) in the heater transfer regulates the amount of fuel gas to the burners from a constant pressure gas line. This results in the feed to the catalyst chambers running at constant volume and temperature, so that even though the olefin content of the gas may not be uniform on account of a varying recycle, the temperature and pressure differentials remain constant. Leaving the catalyst towers the mixture of polymer and gas passes through a condenser and cooler and thence through a pressure control (2) which maintains constant pressure on the outlet of the chambers. The mixture of gas and polymer then passes to the poly stabilizer.

Here setting a hand valve in the water line to the condenser at the top of the tower maintains a substantially constant flow of reflux down the tower.

At the bottom of the tower a temperature controller (3) keeps constant temperature at the vapor return from the reboiler, balancing the heat requirements of the column to take account of changes in quality of feed or of reflux, and keeping a constant vapor pressure on the poly product.

In this operation the cracking plant stabilizer is ordinarily operated as a debutanizer, and at a pressure somewhat below the usual stabilizer producing a specification gasoline. As a result the quantity of polymer product from a given cracking plant may be increased as much as 60 to 70 percent over that which would be produced if the cracking plant stabilizer were making a 10-pound Reid vapor pressure gasoline.

Under these conditions the poly plant stabilizer must save enough butane to bring the cracked gasoline back up to vapor pressure, and it therefore is acting more like a depropanizer at a pressure considerably in excess of the cracking plant stabilizer. This provides an excess pressure so the poly stabilizer pressure control (4) has sufficient differential to be workable and still can discharge into the outlet of the cracking plant stabilizer ahead of the pressure controller in order to provide the recycle. Finally, liquid level control (5) releases polymer to storage for blending with the debutanized gasoline.

The principal requirement for stability in the process is satisfied by provision at the start for a constant flow of gas at constant temperature. Stability is maintained by the use of pressure controllers with relatively wide band throttling characteristics and reset mechanism, in order to keep the control point from wandering. The same type of control is desirable for the reboiler bottom temperature and level so that even though the plant is small and might tend to be sensitive, the operation is smooth.

Where float-type liquid-level controls are used to feed from a receiver to additional equipment, as in the case of the heater of a two-flash topping unit, or the feed to a stabilizer, they should be given maximum throttling in order to keep from setting up hunting. Sizing of control valves is especially important, as an oversize valve limits the working portion of the proportional range, and tends to make the controller sensitive, with a tendency to hunt. Where float-type level controls are used, a horizontal receiver and long arm are of distinct advantage. The receiver then provides greater storage space to take up fluctuations, rather than pass them on, perhaps even accentuated. A long arm on the float ball builds up the power available for overcoming stuffing box friction and resistance of the pilot valve, and also minimizes the effect of lost motion. Even more important from the standpoint of smooth flow is the increased float travel for a given movement of pilot valve. This increases the storage volume available for taking care of fluctuations. For smoothest flow, the instrument type controller with reset has advantages and allows a smaller receiver to be used.

On-and-off controllers, or even narrow band controllers, have little application for level control, unless it be purely for release to storage, and even then they may cause surges. The principal objection to their use is the difficulty of predicting whether they will be applicable in a given case because of lack of a method of coordinating the lags and capacities of the process and the characteristics of the controller.

In any process a tendency toward self-regulation must be taken into account as it may work with or hinder the operation of automatic control equipment. A typical instance of self-regulation is the case of a centrifugal pump with a steep Q-H characteristic curve. When a controller calls for an increased flow by opening a valve in the line, the resulting drop in pressure at the discharge of the pump limits the flow to a figure less than that which would result with a constant pump pressure. The controller must open the valve much wider than would be the case with a constant pump pressure in order to establish the desired new flow condition.

Another instance of self-regulation is the case of a heater with a large amount of exposed refractory surface. This provides a heat storage capacity which has a beneficial effect in absorbing and averaging slight temporary fluctuations in the flow of fuel when the feed to the heater is constant. However, if the rate of feed be increased, resulting in an increase of load, the heat storage capacity must be also increased to correspond to the higher furnace temperature at the new load, and until the refractory surface is saturated with heat at the new temperature level stable firing conditions cannot be attained. With varying flow to the heater, automatic temperature control may become unsatisfactory or even impossible.

TEMPERATURE, PRESSURE, FLOW AND LEVEL

The principal elements subjected to automatic control in topping, cracking and polymerization plants

are temperature, pressure, flow and level. It might be thought that with the passage of years, these controls would become simplified and standardized to a few major items. However, this is not the case. Consider the range of equipment available for control of temperature, from the self-actuated type where the pressure generated in a vapor tension bulb acts on a sylphon bellows on the head of a control valve to open or close the valve, up to the combination of a potentiometric measuring system with a pneumatic or hydraulic relay control system. In the first case the system ordinarily has a wide throttling range (wide band proportional type), and usually is subject to considerable lag due to capacity of the bulb system, and error due to sticking of the valve stem resisting slight changes in pressure in the sylphon bellows. In the second case, a highly sensitive system for the detection of temperature can be combined with a control system of great flexibility, incorporating adjustable throttling range or proportional band, speed of reset, and anticipation.

In between these two extremes are off and on controllers, two position controllers, and relay or pilot operated types using a mercury or vapor-tension bulb for detection, narrow or wide band proportional control and a host of gadgets developed by various manufacturers.

Since a similar wide range of control equipment is available for each of the other elements, pressure, flow and level, it is not to be wondered at that a considerable amount of confusion exists in the minds of engineers or instrument salesmen called upon to specify equipment for a given case.

A few years ago a prominent instrument company advertised that "60 percent of all control problems can be handled by on-and-off control." This statement was no doubt made as the result of a study of a large number of control problems brought to them for solution. However, it is probable that the number of on-and-off controls actually sold is a very much smaller percentage of the total, because of the fact that there is no convenient method of analysis to indicate when this type is feasible. Consequently, the instrument salesman offers and the engineer specifies a more expensive type of control with greater flexibility in order to be able to make adjustments in the field to match up with the existing process capacities, lags, etc.

Level control, although perhaps the simplest of the above systems, has been greatly abused. In an early application of a pilot-operated liquid-level control, approximately one quarter-inch movement of the float ball corresponded to the full travel of the control valve. This controller installed on the bottom of a four-foot diameter tower and operating a valve in the steam line to the feed pump of a cracking unit resulted in upsetting the whole operation. Although the flow of raw charge to the tower was maintained constant, the level controller was so sensitive and the lags were so great that a considerable over-travel resulted, and the level in the bottom of the tower varied six to eight inches, with the process on automatic control. The feed pump ran at full speed for a period of two or three minutes while the level was above the narrow control range, and then shut down completely as the level crossed the range. Addition of air capacity tanks, orifice in the air line to the diaphragm valve, and limitation of control valve operation by by-pass and block valves either showed little overall improvement, or resulted in the necessity of a considerable amount of hand control to keep within an operating range. The operators quickly found that it was simpler to discard the controller entirely and make occasional small adjustments to the steam valve by hand, with a resulting smooth flow to the cracking plant.

Had it been possible to set the controller for a two-foot range of level corresponding to full travel of the valve, fluctuations would have been taken up in the storage volume provided for that very purpose at the bottom of the tower, and the resulting flow would have been very much smoother and the operation satisfactory. However, such a controller was not available at that time.

A more recent application of level control involved a differential instrument type level controller installed on a stabilizer reflux accumulator, operating a valve in the water line to the condenser. Although this controller was provided with an "averaging" or extreme wide band throttling range and reset, the use of this resulted in wandering of the level recorded on the chart. Such a ragged record reflected on the ability of the operator and instrument man, and the controller was speeded up until the level recorded on the chart was practically constant. The release of gas from the accumulator became correspondingly unsteady, although the pressure controller was speedy enough to handle it without noticeable pressure variations. The excess gas was the feed to a polymerization unit, and as a result of the continued variation of feed the poly plant controls had to be set up to cope with such variations, resulting in a sensitive instead of a stable process.

This instance illustrates one of the psychological problems encountered in connection with automatic control. An improved method of handling the problem would have been the use of an indicating controller, with a flow meter in the gas release line.

In practically all level-control problems, the result really desired is not a constant level, but a smooth and uniform controlled flow, with any fluctuations between flow in and out taken up by variations in the

PROPORTIONAL TYPE LIQUID LEVEL CONTROLLER.
AREA OF LIQUID SURFACE - 10 SQ. FT.
NORMAL FLOW - 1000 BBL PER DAY.
MAXIMUM FLOW WITH WIDE OPEN CONTROL VALVE - 2000 BBL. PER DAY.
PRESSURE IN RECEIVER 75 #/SQ. IN.
PRESSURE IN OUTLET LINE AFTER VALVE - 25 #/SQ. IN.
SPECIFIC GRAVITY OF LIQUID - .7
CONTROLLER CHARACTERISTICS ARE SUCH THAT WIDE OPEN PILOT VALVE WILL PRODUCE FULL TRAVEL OF CONTROL VALVE IN 2 SECONDS.

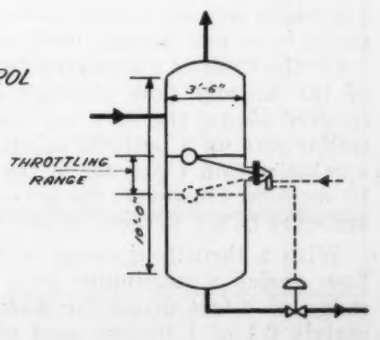


FIGURE 6

Physical Set-Up of Level Controller.

level within the proportional range of the controller. In many cases, the greatest difficulty is to obtain recognition of this principle, after which the problem is easily solved.

Earlier in this paper mention was made of two recent articles on the mathematics of control. An interesting application of the methods indicated by Spitzglass in his second paper[3] is the analysis of the effect on the level and flow from a typical receiver by a pilot operated liquid level controller having various degrees of proportionality.

Figure 6 illustrates the assumed hookup together with the basic data surrounding the system on which the controller works. In taking the dimensions for the height of proportionality at 0.02, 0.2, 2.0 and 20 feet, four rather typical types of controllers are pictured. The first case is that of an extremely narrow range controller, such as the one mentioned above. The second is approximately the typical case of a kidney-ball-float controller which, as a rule, has less than a 6-inch float travel for full operation of the control valve. Case three applies to the internal float installed in a reservoir where a relatively long float arm can be provided. Case four covers the use of the extreme wide band proportional controller without reset.

It should be noted at this point that in practically all cases where the extreme wide band type controller is used reset should also be provided, otherwise variations in load may result in wandering of the level to a point near the limits of proportionality and any further change causes the controller to go on the steep end band, giving practically an on-and-off control until the process is once more brought within control limits.

The curves in Figure 7 particularly illustrate the difference between the various controllers in providing "level control versus smooth flow."

These curves are calculated on the basis of equations given in Spitzglass' paper,[3] assuming a standard disturbance of 20 percent of the normal flow through the control valve. This amounts practically to increasing the flow into receiver for one second by an amount equal to 20 percent of the normal flow. The mathematical analysis then indicates the effect of this rise in level upon the control system and the variations in flow and level resulting therefrom. Since the normal flow into the vessel remains constant outside of this short disturbance, the level and flow vary from an original normal back to the same normal instead of varying along a logarithmic curve which would be the case if the flow in the vessel were changed from one normal value to a new normal value, say 20 percent higher. The method of analysis indicates the type of control and whether oscillations will be set up just as well with this method as when the flow-in is permanently changed, but the curves are somewhat more convenient to handle since they have a straight line as a basis rather than the logarithmic curve from one normal level and flow to a new one.

On the basis of a standard disturbance of 20 percent of the normal flow through the control valve, as covered above, the very narrow throttling range controller sets up a periodic motion which is damped to a value within 1 percent of the normal flow inside of 10 seconds. However, the maximum variation in flow amounts to 6.6 percent of the normal.

With a throttling range of 0.2 feet the controlled flow varies a maximum of 1 percent. A throttling range of 2 feet drops the flow variation to approximately 0.1 of 1 percent and with a throttling range of 20 feet the deviation is 0.01 of 1 percent, or practically negligible.

The disturbance in flow was taken at a sufficiently small value so as not to bring the sensitive level-control system out of its throttling range. This results in the very small changes in level indicated on the curves for all four control systems. It will be noted, from the curves representing deviation of level, that the narrowest throttling range acts so fast that the variation in level is only .00066 foot. On the other hand, the controller with the 20-foot throttling range allows a variation of approximately .0013 foot and this level is very slowly reduced; in fact, the time required to get back to only .1 of the maximum deviation is nearly 1 hour. The reason for this can be appreciated when it is considered that with a proportional range of 20 feet a variation of .0013 foot results in an almost infinitesimal action of the control valve, whereas the maximum deviation in the case of the narrow throttling range controller actually requires 3.3 percent movement of the control valve.

In this particular problem the difference in flow between using 2-foot or 20-foot throttling range is negligible as far as effect on the process would be concerned. Consequently, the indications are that the extreme throttling range control is not necessary. Even if the flow variations were wider the same receiver and simple proportional control could be used to obtain greater damping of flow changes by setting the vessel horizontally. In this case, with an average area of approximately 30 square feet and a float travel of 2 feet there would be approximately 60 cubic feet working storage capacity in the reservoir against the 20 cubic feet capacity in the vertical receiver. The equivalent storage capacity of the extreme throttling controller in the vertical receiver is 200 cubic feet so that it can be seen that a considerable advance in throttling range can be made by simply laying the vertical receiver on its side.

Incidentally, another characteristic in connection with the straight proportional type level controller in the horizontal cylindrical type tank is that the mid-portion of the tank has the greatest area and storage volume per inch of level variation. Consequently, in this range the controller acts slowly to change the flow. As the level is lowered to a point where the surface cross-section is reduced, the control action becomes faster because of a reduced storage capacity per inch of height.

Where large storage tanks are provided as reservoirs to obtain smooth flow and stabilize plant operation, it is desirable to use an internal type level controller with a long float arm to utilize as much reservoir capacity as possible within the proportional range of the control. It should be noted in this connection that the controllers covered are operating on a single-capacity process and that the controller speed of two seconds is reasonably fast. Use of an increased control time lag or of a two-capacity system, such as might result from feeding into the reservoir over a series of bubble trays or side-to-side pans, can easily change the time relationships in the system so that such a disturbance might take the controller outside its proportional range and result in continued oscillation as in the case of the incident mentioned previously.

One item which might be emphasized at this point is the desirability of the use of valve positioners on control valves when using wide throttling ranges. Since small deviations result in very small percentages of change of air pressure to the motor diaphragm

valve, the expected movement of the valve might not be obtained due to sticking for such very small changes in the force on the valve. Accordingly, the valve positioner will keep the control valve alive to the slight changes called for by the control with the wide throttling range.

With reference to the practical side of the level controls illustrated in the above case, the time required to empty the "working reservoir capacity" with no inflow and maximum outflow would be as follows:

Throttling Range, feet.....	.02	.2	2	20
Seconds to Empty Working Reservoir Capacity with Maximum Outflow and no Inflow.	3.1	31	310	3100

For allied level control problems the use of a storage capacity having a time relation to the maximum flow of the order of the different cases given above will give similar control conditions, always assuming that the application is on a single capacity system.

Since only a very few applications really require accurate level control, the use of such equipment where smooth flow is really the desired feature often results in setting up hunting or cycling throughout the process to which the level controller is attached. This hunting may not only affect the operation but makes the duty of other controls on the process doubly difficult and sometimes impossible. Every instrument man has had the experience of being called to look at a temperature controller which was hunting, only to find that it was doing its best to keep up with cycles set up in the process by a level controller at some point which showed no record of its action.

It is hoped that the discussion and examples given above will stimulate further consideration of instrumentation directly in connection with process engineering with a view to the possibility of making changes in process design when necessary to assist in the problem of instrumentation and, hence, assist in the control of the process itself.

[1]Quantitative Analysis of Process Lags by C. E. Mason, American Society of Mechanical Engineers Transactions, May, 1938.

[2]Quantitative Analysis of Single Capacity Processes by Albert F. Spitzglass, American Society of Mechanical Engineers Transactions, November, 1938.

[3]Quantitative Analysis of Single Capacity Processes II, by Albert F. Spitzglass. Presented at American Society of Mechanical Engineers Meeting December 7, 1938.

[4]"Application of Automatic Control in the Oil Industry," by D. J. Bergman. A.S.M.E. Transactions, Vol. 60, 1938, Pages 651-656.

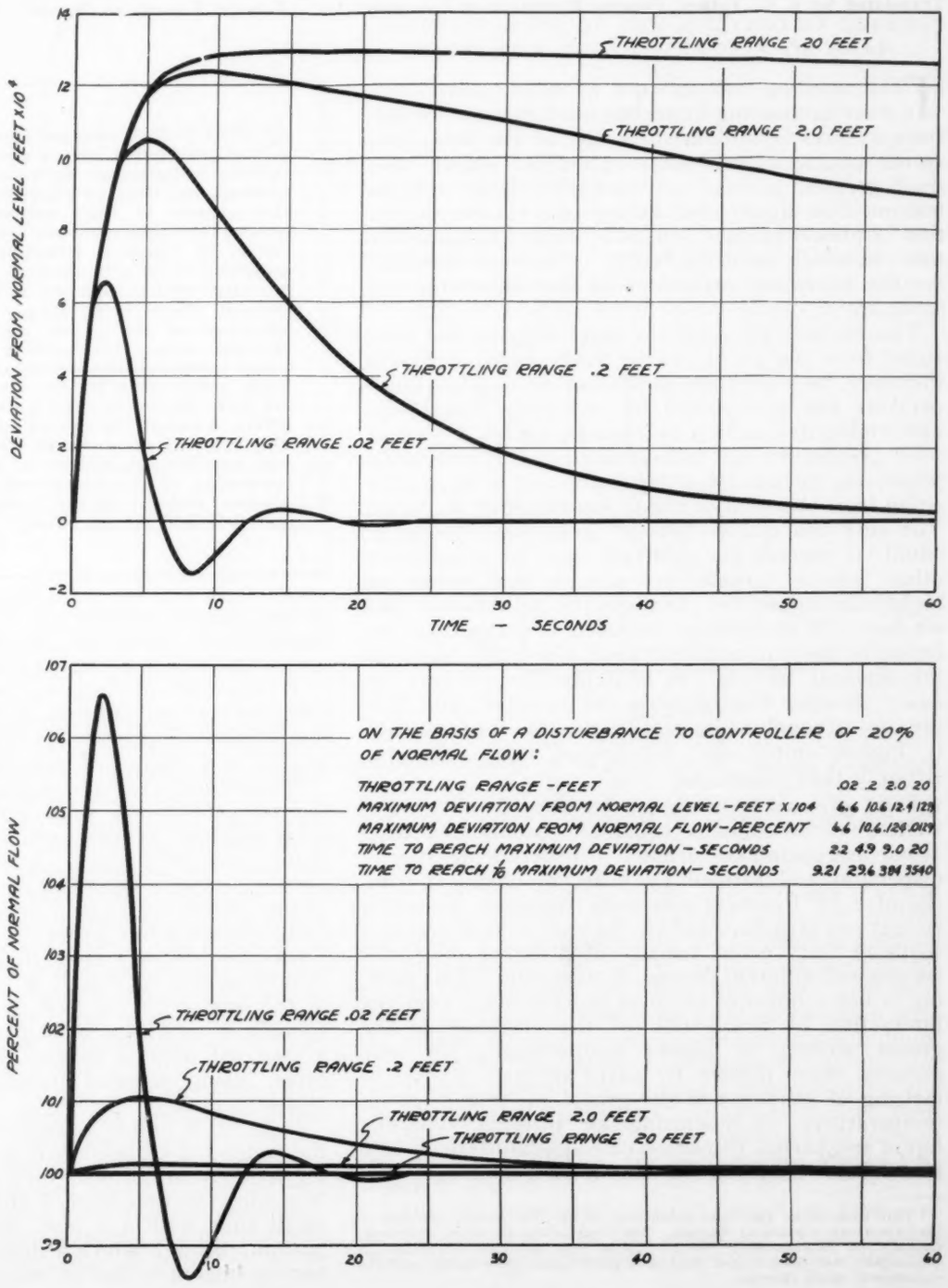

THROTTLING RANGE 20 FEET
THROTTLING RANGE 2.0 FEET
THROTTLING RANGE .2 FEET
THROTTLING RANGE .02 FEET
DEVIATION FROM NORMAL LEVEL FEET X10⁴
TIME — SECONDS
ON THE BASIS OF A DISTURBANCE TO CONTROLLER OF 20% OF NORMAL FLOW:
THROTTLING RANGE - FEET .02 .2 2.0 20
MAXIMUM DEVIATION FROM NORMAL LEVEL - FEET X 10⁴ 6.6 10.6 12.4 12
MAXIMUM DEVIATION FROM NORMAL FLOW - PERCENT 6.6 10.6 12.4 0.19
TIME TO REACH MAXIMUM DEVIATION - SECONDS 2.2 4.9 9.0 20
TIME TO REACH 1/6 MAXIMUM DEVIATION - SECONDS 9.21 29.6 384 3540
PERCENT OF NORMAL FLOW
THROTTLING RANGE .02 FEET
THROTTLING RANGE .2 FEET
THROTTLING RANGE 2.0 FEET
THROTTLING RANGE 20 FEET

FIGURE 7

Effect of Throttling Range of Level Control on Level and Flow.

Melting Point Of Solid Greases*

D. S. VELIKOVSKII, I. P. LUKASHEVICH *and* F. L. BORSHCHEVSKAYA

Neftyanoe Khozyaistvo (The Petroleum Industry) Vol. 19, No. 3, Pages 56-61, March, 1938
Translated by J. G. Tolpin, Process Management Company, Inc., Foreign Literature Service

STRUCTURAL changes brought about by details of production have a pronounced effect on the melting temperature determined by the Ubbelohde method, but have no effect on the performance of the greases at high temperatures. Sodium-base greases are heterogeneous systems, the thermal behavior of which is greatly affected by details of production; in calcium-base greases the effect of the structural pecularities is balanced by the water present. There is no simple relation between the structure of the grease and its stability toward thermal action. The melting point is determined, other factors remaining constant, by the content of soap, rather than by the viscosity of the mineral oil used. The resins exert a stabilizing and peptizing effect. A rise in the valence of the soap base lowers the dropping temperature, the duration of melting and the thermal stability of the grease. Increasing saturation of the hydrolyzed oil or fat raises the thermal stability of the grease, the dropping temperature and the duration of melting.

THE melting temperature of solid greases and other lubricating materials not liquid at ordinary temperatures is still used as one of the basic constants characterizing these materials. Plastic non-fluid greases possess substantially higher internal friction than liquid oils and for this reason application of plastic greases is usually limited to those few cases in which their low fluidity or absence of fluidity are the necessary properties of the lubricating material.[1-a, 2, 3]

The melting temperature characterizing the transition from the plastic to the fluid condition should, therefore, be a constant indicating up to what temperature the grease will be practically capable of performing its function as a plastic grease. However, solid greases are not individual chemical substances possessing an exact melting point and a sharp transition from the solid or plastic condition to the liquid. The very conception "plastic" grease as opposed to "fluid" is exceedingly arbitrary since most solid and other "plastic" greases are actually not plastic but highly viscous bodies; as a specific indication of this we have the air bubbles occluded in greases and released by them in course of time, after they overcome the internal friction[4]. It is impossible to draw an exact dividing line between the non-fluid and fluid greases although some greases possess a substantially higher empirically determined initial shearing strength than others.

Solid greases were shown by one of the present writers[5] to be complex colloidal systems consisting of solvate complexes usually of different degrees of dispersion and formed by different chemical compounds: by hydrocarbons with different molecular weight and structure and (in the case of soap greases) soaps of fatty acids, usually of different molecular weight and different degree of saturation. Their melting is not a uniform physical process but a complex interaction of desolvation of the elements of the grease melting at higher temperatures (in soap greases, those formed by soaps of fatty acids), of melting of elements of the grease melting at lower temperatures, of liberating an internal synaretic liquid and partial transition of colloidal particles into a molecular solution. For this reason melting of the grease usually requires a considerable interval of temperature; while its first signs appear at lower temperatures it is completed at higher temperatures; or it requires a prolonged period of time at the same temperature and consists in the latter case mainly in a thermal dispersion of colloidal complexes accompanied by a sharp fall in internal friction.

All accepted methods of determination of the melting temperature of solid greases actually fix only some arbitrary temperature at which either the first liquid drop of molten (or thermally decomposed) plastic grease is separated from it[6, 7] or a small piece of the grease begins to flow[8] or the grease begins to flow through a fine gauze[1-b]. That all these temperatures are arbitrary is obvious. At the temperature defined as the "melting" or "dropping" temperature of the grease only a part of it can melt or soften, sometimes an insignificant part, while the rest of the grease will remain plastic also at higher temperatures, losing none of its ability to function as a plastic grease.

In U.S.S.R. and in a number of European countries the method of Ubbelohde is used for determination of the temperature of drop formation of plastic greases. According to this method the grease is placed in a small tube with a 3 mm. diameter opening in the bottom, through which a thermometer protrudes, the narrow mercury end of which is inserted into the

* This translation has been submitted by the Petroleum Division of the American Chemical Society. The Petroleum Division, however, assumes no responsibility for the facts that opinions presented in this paper, nor does it nor does this publication necessarily endorse statements made therein.

grease. The thermometer together with the tube containing the grease is placed into an air bath, the temperature of which is raised 1° C. per minute. The temperature is determined at which from the lower open end of the tube a drop of the grease is separated and falls down. It is seen that the method of Ubbelohde, just as other methods described in the literature or in use in the industry, does not characterize the melting of the grease proper, it determines only some arbitrary point.

The object of the present work consisted in establishing the dependence of the melting of solid soap

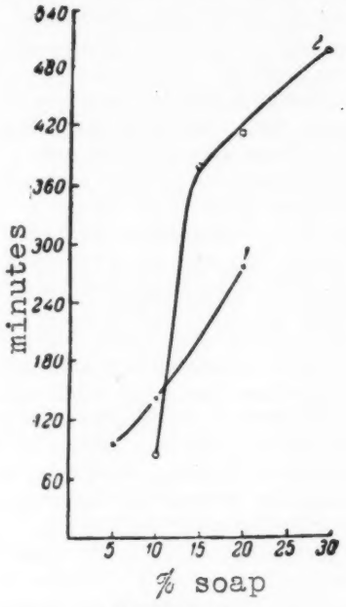


FIGURE 1

Duration of melting. 1—calcium-base grease: 5%—92 min. (54°); 10%—139 min. (87°); 20%—257 min. (102°); 2—sodium-base grease: 10%—71 min. (160°); 15%—375 min. (145°); 20%—407 min. (160°); 30%—494 min. (165°).

greases upon the properties of the raw mterial. In order to obtain data characterizing the actual melting of the greases to a higher extent than the abovementioned "melting and dropping points" two methods were used.

The first method consisted in determination of the melting temperatures of the greases in a standard Ubbelohde apparatus, however, not only the temperature at which the first drop falls was noted but also the interval of time within which at the same temperature at which the first drop fell the entire grease ran out of the tube. The second method used in parallel to the first consisted in the following: 3 g. grease samples were placed on 30x30 mm. glass plates fitted on one side with glass flanges. The plates were put into glass cups under a 5° angle so that the side with the glass flange was on the vertex of the angle. The apparatus was kept in the thermostat at the temperature of the test for a definite period of time. The molten part of the grease gradually ran from the plate into the glass cup. The unmolten part moved down but was retained by the flange. After the grease was kept in the thermostat for a definite time the cup with the molten grease that ran from the glass plate was weighed and the part of the grease was determined that melted under the conditions used. Calcium greases were kept in the thermostat at 50° C., sodium greases, at 100° C.—i.e., at

TABLE 1

Content of Soap in the Calcium-Base Grease, %	Temperature of Drop Formation, °C.	Dropping Temperature, °C.	Content of Soap in the Sodium-Base Grease, %	Temperature of Drop Formation, °C.	Dropping Temperature, °C.
5	50	54	10	156	160
10	77	87	15	140	145
20	87	102	20	158	160
			30	160	165

typical temperatures at which they are mostly used in practice. Preliminary experiments showed that sufficiently definite results are obtained in a 6-hour heating. Parallel studies of the melting of the grease by the two different methods made it possible not only to check the results but also to compare them taking into account the pecularities of melting of the grease by each of the methods used.

(1) DEPENDENCE OF THE MELTING OF GREASES UPON THE CONCENTRATION OF SOAP

The temperature of drop formation and separation of the 3 calcium-base and 4 sodium-base greases prepared from animal fat soaps were determined by the standard method using a Ubbelohde apparatus. They are given in Table 1.

It is seen that the drop formation and dropping temperatures of the calcium-base greases increase with increase in the content of soap. However, this is not the case with sodium-base greases. In spite of the effort to produce identical conditions in the prep-

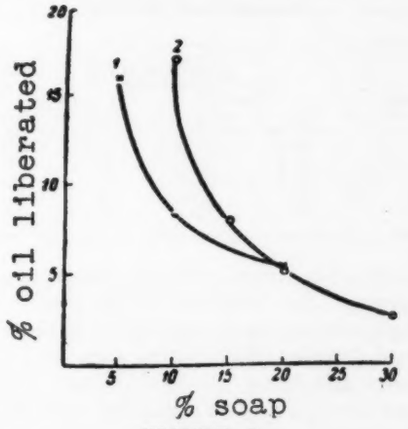


FIGURE 2

Thermal stability. % oil liberated in 6 hours. 1—calcium-base grease: 5%—16% (50°); 10%—8.2% (50°); 20%—5.3% (50°); 2—sodium-base grease: 10%—17% (100°); 15%—8% (100°); 20%—5.1% (100°); 30%—2.66% (100°).

aration of both greases small details in the preparation of the sodium greases greatly affect the melting temperature as determined by the Ubbelohde method. Nevertheless the duration of melting of the greases at the temperature at which the first drop falls shown in Figure 1 reveals its direct connection with the content of soap in the calcium and in the sodium-base greases. The same dependence exists also for the thermal stability of greases determined by the amount of liquid phase separating at elevated temperatures (6 hours at 50° C. for calcium-base greases and 6 hours at 100° C. for sodium-base greases) as shown in Figure 2.

Thus the structural changes resulting from unaccountable details in the conditions of preparation affect the dropping temperatures determined by the

Ubbelohde method and for sodium greases this influence is quite pronounced; the behavior of the greases at elevated temperatures are apparently entirely unaffected. Sodium-base solid greases are strongly heterogeneous systems consisting of conglomerations of gels of different concentrations containing solvate complexes of different degrees of dispersion[5]. Slight changes in the conditions of boiling or cooling change the uniformity of the structure of the greases and may result in formation or disappearance of a small part of the grease that shows a lower thermal stability than its main mass. This affects the

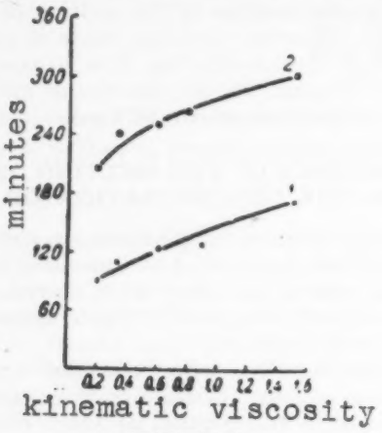


FIGURE 3

Duration of melting of greases prepared with oils of different kinematic viscosities. 1—calcium-base grease; 2—sodium-base grease.

Kinematic Viscosity at 50°C.	E_{50}	CALCIUM-BASE GREASE		SODIUM-BASE GREASE	
		Min.	°C.	Min.	°C.
0.2	3.04	90	78	205	140
0.36	5.15	108	82	240	135
0.58	8.08	122	88	251	132
0.90	12.4	126	96	268	148
1.46	20	172	98	304	16

temperature of formation and separation of the first drop. However, the behavior of the grease as a whole at this high temperature undergoes little change. The behavior of greases of the same composition and prepared under the same conditions but containing different amounts of the same soap, will depend only upon the concentration of the latter. For calcium-base greases it is shown by one of the writers[5] that the peculiarities of the structure are equalized by the action of the surface-active medium—water, that is present outside the solvate envelope, and for this reason the small details in the conditions of preparation do not produce visible changes of the temperature of the formation and falling of the first drop.

(2) DEPENDENCE OF THE MELTING OF GREASES UPON THE VISCOSITY OF THE MINERAL OIL

This dependence was studied on 5 calcium-base and 5 sodium-base solid greases containing 15 per-

1. Bright stock, 100%	Spindle oil, 0%	Kinematic viscosity at 50 °C. 1.46
2. Bright stock, 75%	Spindle oil, 25%	Kinematic viscosity at 50 °C. 0.90
3. Bright stock, 50%	Spindle oil, 50%	Kinematic viscosity at 50 °C. 0.58
4. Bright stock, 25%	Spindle oil, 75%	Kinematic viscosity at 50 °C. 0.36
5. Bright stock, ...	Spindle oil, 100%	Kinematic viscosity at 50 °C. 0.2

cent soap and mineral oils of different viscosity and prepared by mixing bright stock and spindle oil in the following proportions:

TABLE 2

Kinematic Viscosity of the Oil, 50 °C.	E_{50}	SODIUM BASE		CALCIUM BASE	
		Drop Formation Temperature, °C.	Dropping Temperature, °C.	Drop Formation Temperature, °C.	Dropping Temperature, °C.
0.2	3.04	128	140	68	78
0.36	5.15	128	135	76	82
0.58	8.08	116	132	77	88
0.90	12.4	130	148	78	96
1.46	20.0	148	160	88	98

The temperatures of drop formation and drop separation for these greases were as in Table 2.

It is seen that while the temperatures of drop formation and drop separation of calcium-base greases rise with the rise in viscosity of the mineral oil, this direct dependence is not observed in the case of sodium-base greases. Greases prepared with oils of medium viscosity have a lower melting point than greases prepared with more viscous or less viscous oils. It is interesting to note that also in other studies carried out by one of the writers in collaboration with I. P. Lukashevich[9] and with L. S. Shakhoyan[10] it was established that similar extreme values of penetration and other physical properties (adherence, limit of shearing strength) exist for sodium-base greases prepared with oils of medium viscosity in comparison with those prepared with oils of higher or lower viscosity. All this indicates an effect of details of boiling which is not accidental but rather regular structural changes are observed here resulting in lowering of the physical constants.

However, the results of a study of prolonged complete melting of the grease (Figure 3) and of its thermal stability (Figure 4) show no extreme points. The rate of melting and the amount of oil separated

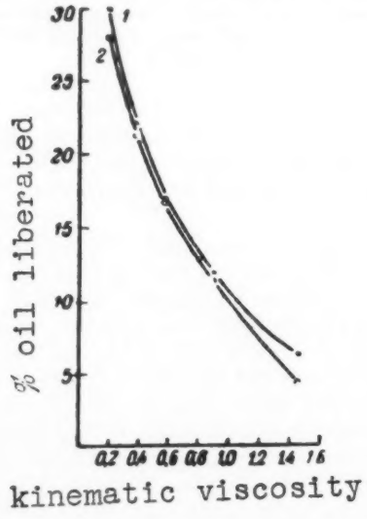


FIGURE 4

Thermal stability. % of oil liberated in 6 hours. 1—calcium-base grease; 2—sodium-base grease.

Kinematic Viscosity	E_{50}	CALCIUM-BASE GREASE		SODIUM-BASE GREASE	
		%	°C.	%	°C.
0.2	3.04	30	50	28	100
0.36	5.15	22	50	21.1	100
0.58	8.08	16.8	50	16.6	100
0.90	12.4	12	50	11.2	100
1.46	20	6.1	50	4.15	100

TABLE 3

Content of Resin by Marcusson, %	SODIUM-BASE GREASE		CALCIUM-BASE GREASE	
	Drop Formation Temperature, °C.	Dropping Temperature, °C.	Drop Formation Temperature, °C.	Dropping Temperature, °C.
0	110	122	96	98
1.1	106	115	97	99
3.06	102	110	98	101
10.2	100	112	84	90

decrease with increase of the viscosity of the mineral oil. Thus, the basic properties of the structure of the grease and its thermal stability show no simple connection. The actual melting of the grease is caused, other factors remaining unchanged, by the amount of soap contained in the grease and to a considerably lower extent by the peculiarities in the structure of the greases that determine the extreme points in the dependence of the temperature of formation of the first drop upon the viscosity of the liquid phase of the grease.

(3) DEPENDENCE OF THE MELTING OF THE GREASES UPON THE DEGREE OF REFINING OF THE MINERAL OIL PRESENT IN THE GREASE

This dependence was studied on 4 sodium- and calcium-base greases prepared with spindle oil distillate, unrefined and refined to different extents by treatment with sulfuric acid and bleaching earths. The extent of refining was judged by the content of resin determined by the method of Marcusson. The

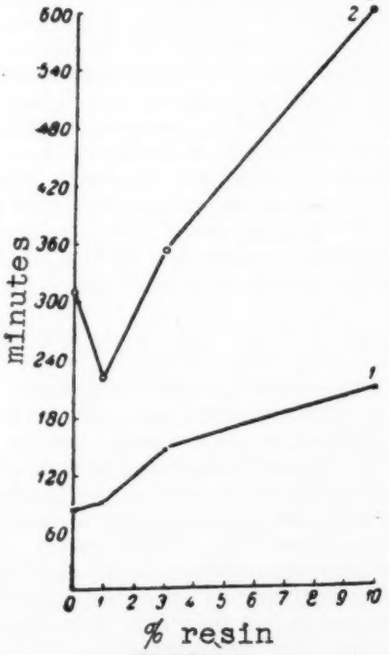


FIGURE 5

Duration of melting of greases prepared from oils with different contents of resins. 1—calcium-base grease; 2—sodium-base grease.

% Resin by the Method of Marcusson	CALCIUM-BASE GREASE		SODIUM-BASE GREASE	
	Min.	°C.	Min.	°C.
0	84	98	312	122
1	90	99	324	115
3.06	148	101	355	110
10	206	90	605	112

greases had the following temperatures of drop formation and drop falling as determined by the method of Ubbelohde.

Different results for sodium- and calcium-base greases are obtained also in the present case. However, while a symbatic dependence of the temperature of formation and of falling of the first drop was previously observed for calcium-base greases and an absence of such a symbatic dependence for sodium-

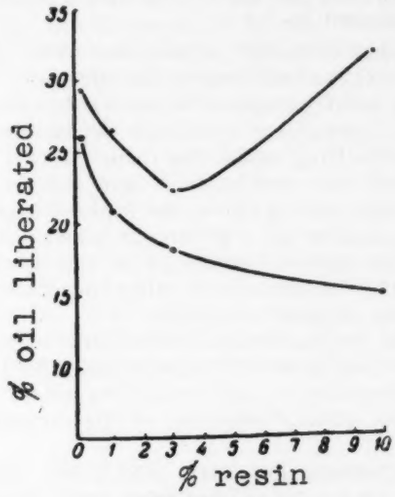


FIGURE 6

Thermal stability. % oil liberated in 6 hours from greases prepared from oils with different contents of resins. 1—calcium-base grease; 2—sodium-base grease.

% Resin by the Method of Marcusson	CALCIUM-BASE GREASE		SODIUM-BASE GREASE	
	%	°C.	%	°C.
0	29.1	50	26	100
1	29.6	50	20.7	100
3.6	22.2	50	18	100
10	31.2	50	15	100

base greases, the reverse is observed in the present case. The temperature of formation and falling of the first drop for sodium-base greases increases with increase of the content of resins in the grease (a small increase in the dropping temperature of the grease with 10.2 percent resins does not affect the principle). For calcium-base greases an extreme development of this dependence is observed and with a low content of resins the temperature of drop formation and of drop separation increases with the increase of the content of resins but shows a sharp reduction when the content of resins reaches 10.2 percent.

However, the behavior of the calcium-base greases should be regarded as showing a definite regularity since a small resin content exerts a stabilizing effect and a substantial content of resins produces a peptizing effect. In case of sodium-base greases where the homogenizing effect of water is not present resins always act partly as peptizers, being at the same time stabilizers. A comparison of the temperatures of formation and falling of the first drop of these greases with their thermal stability (Figure 6) completely confirms these assumptions. For the thermal stability of the calcium-base greases a curve is obtained with an extreme point showing the highest stability corresponding to a 3 percent content of resins, but for sodium-base greases a rise in stability is observed

with increasing content of resins in the grease. Instead of the symbatic we observe an antibatic development of the dependence of the temperature of formation and the temperature of separation of the first drop on one hand, and the thermal stability on the other hand upon the resin contact: a rise in the content of resins reduces the temperature of drop formation and falling but the amount of oil liberated is also reduced. This is totally explained by the partly peptizing but on the whole stabilizing effect of the resins mentioned above.

A somewhat different picture was observed in the study of the rate of melting at the dropping temperatures of the same greases (Figure 5). In this case for calcium-base greases a symbatic dependence of the duration of melting upon the resin content was observed, while for sodium-base greases an extreme point is present in the curve, the highest rate of melting corresponding to a 1 percent content of resins. However, the general tendency is the same also in this case: the duration of melting increases with increase of the content of resins.

Thus, the peptizing and stabilizing effect of the resins is beyond doubt. The peptizing effect is a further manifestation of the stabilizing effect which is shown in the general behavior of the greases.

(4) DEPENDENCE OF THE MELTING TEMPERATURE OF THE GREASES UPON THE SOAP BASE

To study the effect of the soap base in the grease on its melting point, greases were prepared containing 25 percent of salts of stearic acid; sodium, calcium and aluminum salts were used as representing monovalent, divalent and trivalent metals. The temperature of formation and falling of the first drop in the Ubbelohde apparatus were as follows:

	Drop Formation Temperature, °C.	Drop Falling Temperature, °C.
Sodium-Base grease	118	126
Calcium-base grease	98	104
Aluminum-base grease	98	96

The duration of melting of these greases at the temperature of formation of the first drop is graphically shown in Figure 7 and their thermal stability in Figure 8.

The temperatures of formation and falling of the first drop is reduced with increase of the valence of the cation. Similarly the duration of melting is reduced with the increase of the valence of the cation. Finally, the same picture is observed with regard to the thermal stability. Although the sodium-base grease was kept in a thermostat at 100° because of its higher melting point, while the calcium- and

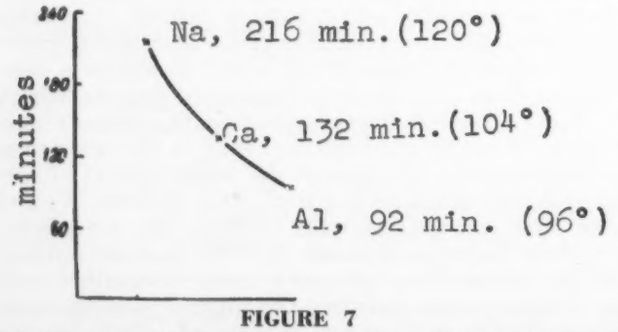


FIGURE 7

Duration of melting of greases prepared with soaps of different bases.

TABLE 4

Fat Used for the Grease	Iodine Number of the Fat	Drop Formation Temperature of the Grease, °C.	Dropping Temperature of the Grease, °C.
1. Animal fat	74.1	88	98
2. Cottonseed oil	127.7	66	75
3. Linseed oil	213.7	62	71

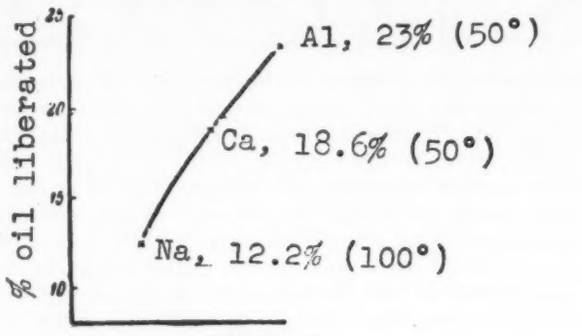


FIGURE 8

Thermal stability. % oil liberated in 6 hours from greases prepared with soaps of different bases.

aluminum-base greases were kept at 50°, the sodium-base grease liberated less oil than the calcium and the calcium less than the aluminum-base grease.

(5) DEPENDENCE OF THE MELTING OF THE GREASES UPON THE DEGREE OF SATURATION OF THE HYDROLYZED FAT

To study the effect of the extent of saturation of the hydrolyzed fat from which the soap used for the grease was prepared, 3 calcium-base greases were made from the soaps of the oils shown in Table 4.

Figure 9 shows the duration of the melting of the grease at the dropping temperature. Figure 10 shows the thermal stability of the greases at 50° C.

A complete analogy is observed in the 3 series of determinations. A reduction of the iodine number brings about a rise in the temperatures of formation and falling of the first drop, a rise in the duration of the melting and a reduction of the amount of oil liberated in the thermostat (increased thermal stability).

Sodium-base greases were prepared with soaps from the following oils in Table 5.

In each of the three greases 15 percent of one of the above soaps were used and refined spindle oil, the boiling being uniformly carried out for 1.5 hours at 150-160°. It is interesting to note that a prolongation of the boiling and a rise in the temperature of boiling increases the temperatures of formation and of falling of the first drop of the greases in the same way as the duration of the melting and the thermal stability; this increase is more pronounced in the cases of greases made with fats of a higher degree of unsaturation. Thus, the quantitative differences for greases made with oils of different extent of saturation decrease but the order remains the same. Prolonging the duration of boiling and increasing its

Table 5

Fat Hydrolyzed in the Soap for Grease	Iodine Number of the Fat	Temperature of Drop Formation of the Grease, °C.	Dropping Temperature of the Grease, °C.
1. Tallow	56	137	148
2. Cottonseed oil	127.7	85	125
3. Linseed oil	213.7	70	103

temperature also reduces the interval between the temperatures of drop formation and drop falling which indicates a high uniformity of the colloidal structure of the grease formed in this case.

In case of sodium-base greases boiled under the same conditions, no matter what these conditions were the same dependence of the duration of melting and thermal stability is established upon the extent of the saturation of the fat as was observed for

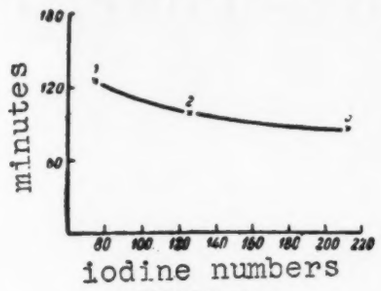


FIGURE 9

Duration of melting of calcium-base greases prepared with soaps of fats with different iodine numbers.
1— 74.1 (animal fat) 124 min.;
2—127.7 (cottonseed oil) 100 min.;
3—213.7 (linseed oil) 88 min.

the calcium-base greases: a rise in the saturation of the saponified fat results in an increase of the thermal stability and the duration of the melting of the grease at the dropping temperature.

CONCLUSIONS

Physical and chemical factors exert different effects on the melting of solid greases.

(a) Chemical factors, i.e., the extent of saturation of the fat and the valences of the soap base in the grease produce the same picture when the melting of the grease is studied by any method. A symbatic dependence is established upon these factors of the temperatures of formation and separation of the first drop, of the duration of melting at the dropping temperature and of the thermal stability. The temperatures of formation and falling of the first drop are reduced, the duration of melting of the dropping temperature is also reduced and the amounts of oil liberated on keeping the grease in the thermostat increase (thermal stability diminishes) with increase of the degree of unsaturation of the hydrolyzed fat and rise in the valence of the soap base.

(b) Physical and colloidal factors such as concentration of the soap in the grease, viscosity of the liquid phase of the grease (mineral oil), the extent of refining of the mineral oil (i.e., change in the content of surface-active substances) produce no similarity of effect in the study of melting of the grease by different methods.

No direct dependence is observed between the temperatures of formation and falling of the first drop and (1) concentration of the soap in the sodium-base greases; (2) viscosity of the mineral oil in sodium-base greases; (3) extent of refining of the mineral oil in sodium- and calcium-base greases. This was properly explained but no practical way is given of judging the actual behavior of the greases from the temperatures of drop formation and drop falling.

The duration of melting of the grease at the dropping temperature increases with increase of the concentration of the soap in the grease and also with increase of the viscosity of mineral oil in calcium- and sodium-base greases. A similar dependence is established for the thermal stability which rises (the amount of oil liberated diminishes) with increase of the concentration of the soap and of the viscosity of the mineral oil.

The extent of refining of the mineral oil differently affects the duration of melting of the grease at the dropping temperature and the liberation of the oil in the thermostat (thermal stability). For calcium-base greases a curve with an extreme point was obtained for the dependence of the thermal stability upon the extent of refining of mineral oil and a curve showing a gradual rise was obtained for the dependence of the duration of melting of the grease upon the extent of refining of the oil. For sodium-base greases an antibatic development of the dependence of the temperatures of drop formation and drop falling and of the thermal stability was established, but the latter produces a curve showing a gradual decrease with increasing extent of refining. The duration of melting is also increasing with the decrease of the extent of refining (increase in the content of surface-active ingredients removed by refining), but this is shown by the obtained curve in a less definite way.

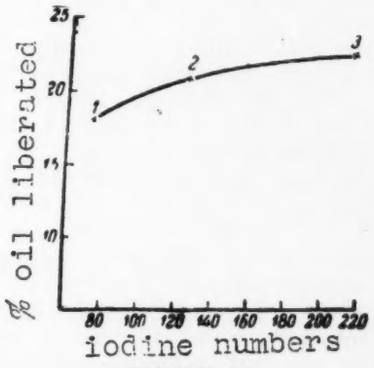


FIGURE 10

Thermal stability. % oil liberated in 6 hours from greases prepared with soaps of fats with different iodine numbers.
1— 74.1 (animal fat) 18%;
2—127.7 (cottonseed oil) 21%;
3—213.7 (linseed oil) 23%.

The difference in the behavior of calcium-base and sodium-base greases is explained by the action of the surface-active medium (water) present outside the solvate in the calcium-base greases and equalizing the structure of the grease. Determination of the thermal stability of greases in the thermostat characterizes them in a way that approaches most closely their actual melting. A corresponding constant should be evaluated and its conditions (temperature of the test, duration, permissible percentage of liberated oil) should be established and substituted for the dropping temperature of solid greases.

LITERATURE REFERENCES

[1] E. N. Klemgard, "Lubricating Greases" (Russian translation) Moscow, 1931 (1-a, page 43; 1-b, page 68).
[2] Garlin, "Lubricating Greases" (Russian translation) Baku, 1936.
[3] D. S. Velikovskii, "Quality and Application of Solid Greases," Moscow, 1937, page 7.
[4] Rhodes and Allen, J. Ind. Eng. Chem. 25, 1275 (1935).
[5] D. S. Velikovskii, Trans. Conf. Lubricating Greases (in print).
[6] Gillette, J. Ind. Eng. Chem. 1, 351 (1909).
[7] Holde, "Fats and Oils" (Russian translation) Leningrad, 1931, page 53.
[8] Cook, Proc. Chem. Soc. XIII, 74 (1897).
[9] D. S. Velikovskii and I. P. Lukashevich, Trans. Conf. Lubricating Greases (in print).
[10] V. S. Velikovskii and L. S. Shekhoyan, unpublished work, Moscow Petroleum Research Institute.

Steam *at Low Cost*

In Wilshire's Power Plant

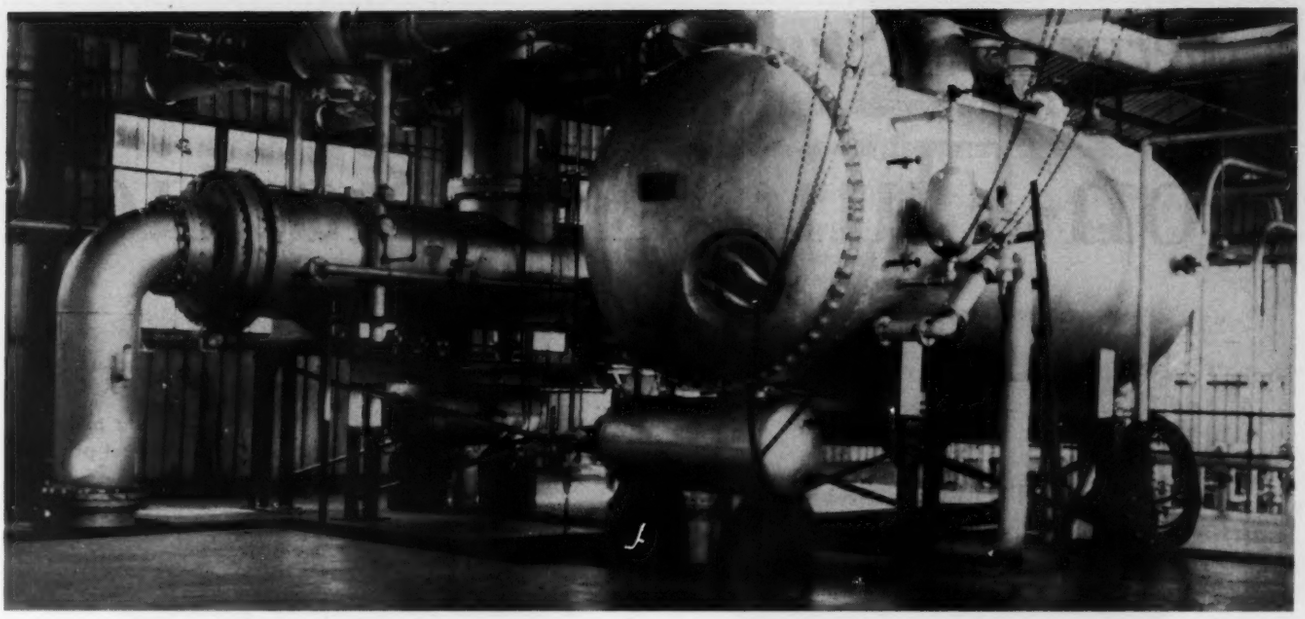
J. C. ALBRIGHT

WITH certain improvements in its refinery at Norwalk, California, Wilshire Oil Company now operates a controlled system for generating and distributing steam at an overall cost of less than 15 cents per thousand pounds. The steam-generating plant installed when the new refinery was constructed less than three years ago consisted of four bent-tube, three-drum boilers having a generating capacity of 30,000 pounds per hour in each unit. Due to changes in the hot-oil pump installation, when three high-pressure, high-superheat steam turbines were installed to operate multi-stage charging pumps for the cracking unit, a fifth boiler was installed, having a capacity of 50,000 pounds per hour. The top capacity of the steam plant is now 170,000 pounds per hour, which is superheated to 560° F. for direct use in the first stage of consumption, mainly in steam turbines operating water pumps and in the tubines driving the hot oil charge pumps.

The steam as it leaves the boiler drums has a saturated temperature of 450° F. at 450 pounds, gauge, but is piped through integral superheating tubes before release to the distribution header to increase the efficiency of the turbines which drive the large pumps. The consumption of steam for November, 1938, was 68,703,000 pounds over the 30-day period which cost the company $8210 for the month. This cost was at the rate of 11.95 cents per thousand pounds and included operating charges, maintenance, depreciation and amortization.

The steam is carried throughout the plant in three systems; in the first the 450-pound steam at 560° F. flows to the water pumps, the hot-oil-charging pumps and the auxiliary equipment in the boiler room that require steam at this pressure and temperature. Through a system of compensating valves, exhaust steam from the high-pressure turbines is discharged into the intermediate header for use in reciprocating pumps and a few low pressure turbines. Exhaust from these units is discharged into a third system which carries the steam back to the boiler room for condensation. During the passage of steam from one system to another, the compensating valves function to permit high-pressure steam to enter the intermediate system if the exhaust from the high-pressure turbines is insufficient for the immediate require-

Recently Installed Integral Furnace Boiler



Evaporator and Condenser in Wilshire Oil Company's Norwalk Refinery

ments of this system. At another point the low pressure steam is supplemented by either high-pressure steam or intermediate steam, or both, if necessary. The high-pressure, high-supeheated steam, when handled by the compensating valves, flows through a desuperheater to permit use in either of the other two systems.

The functioning of the controls in the three systems is so closely adjusted that no matter what the requirements of either of the lower-pressure systems, nothing is thrown out of balance. Any pump may be taken out of service on the high-pressure or intermediate systems and the recording pressure pens will continue to draw a continuous concentric line on the charts. If a sudden demand is made for steam in the refinery at any point, the compensating valves in the systems will function immediately and supply the correct amount to supply the needs of the unit in use.

Five centrifugal pumps are located in the boiled room. They are at this point in the plant to insure a plentiful supply of high-pressure steam, and they handle all the refinery cooling water. One of the largest atmospheric cooling towers on the west coast is used to cool 20,000 gallons of water per minute from plant temperature to an average of 86° F. Three high-pressure steam turbines driving the multi-stage charging pumps handle the necessary hot oil for an overall plant charge of 15,000 barrels per day.

Water for the boiler room and plant consumption is produced from three deep wells which have a combined capacity of about 3000 gallons per minute with a hardness of 8 grains per gallon. The water required for make-up in the boiler feed system is first treated in a zeolite type softener, passing immediately to a de-aerator, thence to an evaporator, filter and boiler-feed storage. The water is pumped from storage through a second de-aerator and fed to the boilers by multi-stage centrifugal pumps driven by steam turbines. About 40 percent of the water fed to the boilers consists of fresh make-up to take the place of steam used for processing oil in the plant which cannot be used again.

Through condensers and other medium of exchange, the feed water is pumped to the boiler economizers at a temperature of 225° F. and after flowing through these units, enters the boiler drums at a temperature of 325° F. One master meter controls the amount of water required for all five of the steam generators, the amount of fuel, whether gas or residual fuel from the cracking plant, and the amount of air to the burners and the speed of the induced-draft fans.

The building in which the boilers, pumps and auxiliary equipment are located is constructed of steel, large enough to accommodate all necessary units relating to steam generation, with sufficient additional space for operating without undue crowding. The four original boilers are placed, two to each row in the west end of the building and the new and larger unit installed on the south side near the first installation.

The instruments for controlling the flow of fuel, water and air are grouped on a common control board where the boiler fireman may check all operations from one point. The boiler feed pumps are placed as closely to the boilers as practical, and the water circulating pumps and utility units are located at the opposite end of the building. The five water pumps which handle the water cooled over the large aerator, discharge through the steam condenser with an outlet temperature of 110°F. by a continuous circulation system, with this water rising to about 20 grains per gallon temporary hardness in about 30 days. Three 14x10¼x12-inch steam-driven reciprocating fire pumps are located in the end of the boiler room adjacent to water-treating pumps and the pumps used to pass the boiler-feed water to the supply tanks.

A single-stroke, large capacity lubricator supplies lubrication to all required bearings and pumps in the end of the building where the five water-circulating pumps are located. This unit is located next to the wall of the pump section of the boiler room and is driven with an electric motor. The lubricant is piped to the pumps under pressure and fed to the machines through an individual sightfeed unit which may be adjusted manually.

Experimental Studies on

Non-Fluid Lubrication

PART II

High Temperature Reactions of Addition Agents. A. Acid Effects and the Mechanism of Seizure.

S. KYROPOULOS

California Institute of Technology, Pasadena

EXPERIMENTS are described showing that in the region of non-fluid lubrication of greatest practical importance, i.e., that type of lubrication where wear occurs and seizure is liable to occur, chemical high-temperature reactions between the lubricated surfaces and the lubricants are of paramount importance with regard to wear and seizure. The effect of addition agents depends primarily on their chemical characteristics and concentration and on the properties of the products of reaction with the surfaces, not on their adsorption characteristics.

1. *General possible effects of addition agents and outlines of experiments*—In a preceding paper[1] the mechanism of interference of wear (as well as any solid particles dispersed in the lubricant) with the finish of lubricated surfaces was discussed on an experimental basis. The flow of molecules essentially orientated with their long axes in the direction of flow due to flow orientation past boundary layers of the same molecules with essentially perpendicular orientation of their long axes results in contact potentials on the surfaces. The phenomenon is well known as "frictional electricity" when two media of different dielectric constants are rubbed together. Even identical molecules orientated with respect to each other at an angle, as described above, constitute two media of different dielectric constants due to their dielectric dissymmetry. In the case of commercial oils the dielectric difference is greater due to selective adsorption at the solid surfaces. The resulting electric field between the boundary layer and the bulk of the oil makes dispersed particles stick to the solid surfaces, creating there an artificial roughness which promotes more wear.

As in the case of gasoline, the electric fields are weakened according to the electric conductivity imparted to the oil by ionizable or ionizing agents added to the oil or left therein after the various refining processes. An ionizable addition is a compound which may disintegrate into ions, e.g., a fatty acid; an ionizing agent is a compound which weakens the attracting electrostatic forces between ions of opposite signs by its high dielectric constant until they dissociate, e.g., water or acetone. In actual service a non-conductive oil will be more likely to permit roughening of the lubricated surfaces in imperfect fluid lubrication than the same oil with a "conductivity agent." Measurement of non-fluid friction would yield higher values in the former case than in the latter because it would include the mechanical work spent on scratching the surfaces and in current terminology the conductive oil would be called the "oilier" one.

An examination of the compounds which have been tried or studied as potential addition agents from the developed point of view shows that they fall in the two classes as explained above. This already explains failure and success to a certain extent and shows why a high degree of polarity of a particular agent must not necessarily result in improved performance. A comparison between a ketone and an ester may serve for explanation. In general, the ketone will have the higher accessible electric moment (as a matter of fact both types of molecules have not well accessible moments) and will tend to ionize any ionizable compound present, while an ester is indirectly ionizable itself by its transformability into acid under the saponifying influence of water which cannot be excluded under practical service conditions. Thus, ignoring halogenated esters for the present, even the simple representatives must show in practice a dual effect: the physical effect of conductivity and the chemical effect of acid action, i.e., dissolving power for metals.

Thus, the discussion of our investigations leads to several new problems:

1. The part of water as a chemical and ionizing agent;

2. Chemical reactions with extreme pressure lubricants and the transition from physical to chemical action with "ordinary" addition agents, i.e., their potential extreme pressure lubricant action, to which we may add the question: are there any indications of direct reactions between such agents and the metal surfaces? And if there are such reactions, they should be proportional to the concentration of the addition, which calls for an investigation of the lubricating characteristics of *straight* additions. Thus we arrive at:

3. Lubricating properties of straight addition agents with the exclusion of acid effects.

If phenomena of static friction and surface orientation play a decisive part in practical non-fluid lubrication the lubricating properties of addition agents should be, upwards from a few percent, at least nearly independent of concentration. A dependency of friction on concentration would point to a radically changed surface, i.e., chemical reaction with the surface.

Experiments were run in the apparatus described in the preceding paper and the same metallographic method

Wear Prints of neutral and acidious oils obtained on surfaces of different roughness

Figures 1-3: Selected specimen with very smooth surface.
Figures 4-5: Specimen roughened with fine emery perpendicularly to running direction of journal previously to test.

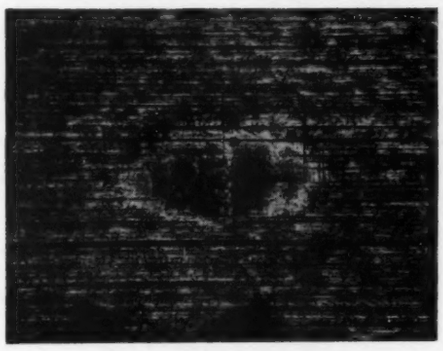


FIGURE 1 (140)
Mineral oil SAE 30 straight 4, 5 h run, direct illumin. 32 x, neutral; wear print on smooth ring.

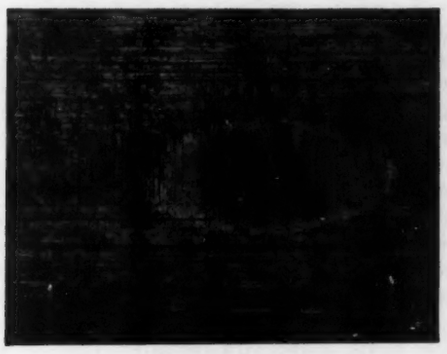


FIGURE 2 (142)
Same oil + 2.5% phenylstearic acid 4 h run, direct illumin. 32 x, acidious; scratched wear print on smooth ring.

FIGURE 3 (145)
Same oil + 2.5% dichlorostearic acid 7, 5 h run, direct illumin. 32 x, more acidious: more scratched w.p. on smooth ring.

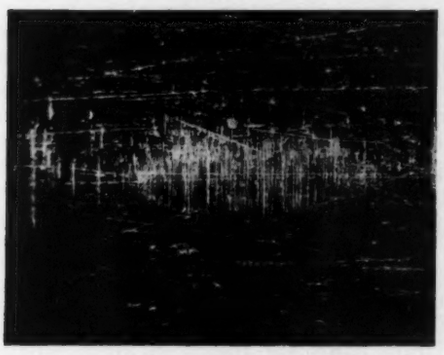


FIGURE 4 (147)
Mineral oil SAE 30 straight 4, 75 h run, dark field illum. 32 x, neutral: heavily scratched wear print on rough ring, negligible chemical action.

FIGURE 5 (148)
Same oil + 2.5% dichlorostearic acid 4, 5 h run, dark field illumin. 32 x, acidious: less scratched w.p. on rough ring due to chemical action.

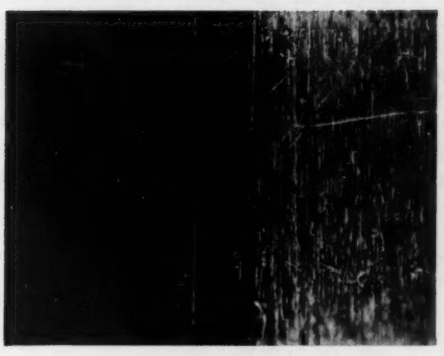


FIGURE 6 (185)
Surface of Falex pin, left half polished by running in with ester from paraffin wax, right half original ground surface. Dark field illum. 32 x.

of examination was used. The investigation was supplemented by quantitative experiments with the Faville-Levally (Falex) lubricant-testing machine on seizure. In a later paper torque-pressure curves obtained with that machine shall be discussed and photo-micrographs showing various surface reactions characteristic of the chemical nature of the various lubricants.

2. *Dissociation and secondary reactions of addition agents*—These effects shall be dealt with in a few typical extreme cases. The effect of dissociation shall be demonstrated by comparing the extreme pressure lubricant effect of an ester and a soap of α-dichlorostearic acid. The ester is saponified at high temperature in the presence of water or contains a very small amount of acid. Due to the negative charge of the COO-group the Cl atom bonds are greatly loosened and become available for the formation of HCl with neighboring H atoms or for direct extreme pressure reactions. Thus we find 0.75 percent of the ester ineffective in the Weeks test. In the case of the soap, due to the strength of the acid, we have complete dissociation, i.e., the highly reactive anions *directly* available. For a soap content of 1.5 percent the Weeks value jumps from 0 to 10 weights, showing that the active ingredient is much more concentrated in the case of the soap. Later quantitative tests with the Falex machine on oil blends of strictly comparable ester and soap concentrations confirmed this result, which shows, incidentally, that the effect is not a phenomenon of surface orientation or what is often called in technical literature "film strength."

The effect of varying strengths of acids is demonstrated by experiments with the wear-test apparatus described in the preceding paper and shown in Figures 1-5. With low effective bearing pressures, i.e., smooth surfaces and consequently essentially fluid lubrication a straight mineral oil will have little tendency of wearing off larger particles and the surface will wear smoothly. An oil containing acid will tend to loosen larger particles by its etching effect, resulting in a less smooth surface. Figures 1-3 show this effect of increasing roughness in the order: straight oil-phenylstearic acid and dichlorostearic acid blend. Figures 4 and 5 show for mineral oil and its dichlorostearic acid blend that the reverse relation holds for rough surfaces, where large particles are broken off whose scratching effect is largely offset by the chemical action of the addition agent but unimpaired by the inactive straight mineral oil. The pictures are, incidentally, a demonstration of the different lubrication requirements of surfaces of different smoothness (running-in process!). By the addition of bases it is possible to counteract any corrosive bulk effects even of powerful extreme-pressure lubricants without destroying their extreme-pressure activity. This was shown in a simple rather crude experiment on the oil containing 1.5 per cent soap of dichlorostearic acid. After adding as much as 3 percent dicyclohexylamine the Weeks test value dropped from 10 to 5 weights as an average of 6 tests. This observation may be useful with respect to the selection of materials for the design of such pieces of machinery which require so-called corrosive extreme pressure lubricants.

A very powerful extreme-pressure lubricant may be deprived of its corrosiveness *in bulk* without losing its desirable properties by adding an amine.

The preceding experiments demonstrate various aspects of chemical reactions which may occur in non-fluid lubrication. First, metallographic inspection reveals acid action under operating conditions while such action is absent under conditions of rest. Second, this action appears as a highly localized action because it does not appear as a corrosion of the whole surface of the wear print. Third, a comparison of the performance of chlorinated ester and anion indicates intermediary local reactions and their different behavior as suppliers of chlorine as would be expected from the different degree of bonding of the chlorine atom. These chemical effects under conditions which must still be termed conditions of boundary lubrication in antithesis to typical extreme-pressure lubrication, definitely dominate here in comparison with effects of non-fluid friction of adsorption layers. This is the essential point. Because if boundary-layer friction were the essential phenomenon, the ester and the anion of its acid should have, at least nearly, the same effect. We may anticipate here a later result, according to which an acid-free non-chlorinated ester shows vastly superior lubricating power in comparison with the same ester with an acid content of the magnitude occurring in commercial products.

TABLE 1
Seizure tests obtained with Falex machine

	Lubricant	Seizure at Lbs.
	Mineral oils straight:	
1.	SAE 20 western solvent ref.	700-800
2.	SAE 50 western solvent ref.	775
3.	SAE 30 Pennsylvania	765
	Mineral oils + additions:	
4.	SAE 20 (No. 1) straight, base oil	650
5.	Same, dried with natural gas	694
6.	Same + 3% ester from paraffin wax not dried	747
7.	No. 6 dried with natural gas	938
8.	No. 6 dried with carbon dioxide	830
9.	No. 4 + 1.5% methyldichlorostearate	926
10.	Same dried with natural gas	916

Thus the question arises whether the main effect of addition agents does not consist in chemical high-temperature surface reactions. With this point in mind various oils and oil blends were dried in different ways and these oils and straight addition agents were tested in the Faville-Levally machine.

3. *Surface reactions and seizure with various addition agents*—In that machine two V-shaped steel jaws are pressed with automatically increasing pressure against a rotating ground steel pin immersed in the lubricant. Total pressures and torques are indicated by a pair of gauges. For the present purpose the pressures at the point of seizure or break were measured. The data are presented in Table 1. In a later paper torque-pressure curves will be discussed. Experiments showed that prepolishing (Figure 6) of the pins by running them in to 750 pounds with a commercial ester, prepared from paraffin wax, yielded better checking results. As a precaution the pins and jaws were electrically connected. The specimens were covered with the lubricants for 10 minutes before use. The values of the table are the average values of at least 5 experiments, in general checking within 2 percent. Differences up to 20 percent result from different setting of the machine or may result from different batches of specimens because of the importance of their surface structure. Only comparable measurements are grouped together.

The data of Table 1 show: approximately same Falex value for oils of different viscosity and origin; slight improvement by drying. For oil with ordinary ester addition: small improvement with 3 percent ester, greater on drying this blend, the value rising to the value of the chlorinated ester blend with its typical extreme-pressure action. No influence of drying in that latter case; specific influence of carbon dioxide.

A marked influence of the chemical nature of the gas atmosphere in experiments on dry friction has been found by Holm and Kirschstein,[2] and by Donandt[3]

TABLE 2

Seizure tests obtained with Falex machine

LUBRICANT	Boiling Point Deg. C.	Seizure, Lbs.	Active Group
Mineral oil SAE 20 straight	....	800	.....
Same + 3% ester from paraffin wax	....	900	—COO—
Same oil + H_2S	....	660	.....
Squeaks at 350 lbs., jaws black on prolonged run	....	....	.....
Same oil + CO	....	640	.....
Same, slowly run in	....	750	.....
Same oil + H_2	....	625	.....
Same oil + O_2	....	830	.....
Mineral oil SAE 50 straight	....	775	.....
Same + CO_2	....	975	.....
Mineral oil SAE 20 + NH_3	....	370	.....
Same, slowly run in	....	1200	.....
Aniline	....	550	—NH_2
Triamylamine	....	440	.....
Same, slowly run in	....	563	.....
Dicyclohexylamine	....	750	.....
Stearonitrile	....	940	C:N
Diethylcarbonate	127	800	—COO—
Butylpropionate	146	480	"
Ethyloxalate	193	750	OCO
Butyloxalate	251	750	OCO
Methylstearate	....	1200	—COO—
Dimethylsebacate	....	1525	2X—COO—
Dibutylsebacate	....	1600	" "
Cetylpalmitate	....	1865	—COO—
Methylphenylstearate	....	1760	"
Methylbenzoate	217	847	"
Ethylbenzoate	200 ?	1010	"
Methylphthalate o.	285	725	2X—COO—
Butylphthalate o.	335	1180	" "
Methyloleate pure	....	2385	C:C—COO—
Same acidious	....	1615	" "
Ester from paraffin wax, pure (acid free)	....	> 2500	—COO—
Same acidious, commercial	....	1600	"
Phenylstearic acid	....	1300	COOH
Oleic acid	....	1800	C:C COOH
Stearyl alcohol	....	1145	COH
Xylylheptadecylketone	....	855	C:O
Mineral oil SAE 30 containing ca. 2.5 percent S (commercial motor oil)	....	1060	.....
Same oil after treatment with silver (cold)	....	790	.....

(carbon dioxide), while Fink and Hofmann[4] described the phenomenon which they called "frictional oxidation," found under conditions of impaired lubrication. Finally Schottky and Hiltenkamp[5] investigated the case of the formation of nitride on steel under similar conditions in the presence of nitrogen.* Obviously this reaction should be particularly easy to observe because the formation of iron nitride takes place already at comparatively low temperatures and the compound, because of its hardness, is liable to change the frictional properties of the surface radically. Thus, drying with natural gas is in the case of oils the most neutral method and the only, in our case, where no foreign matter is added to the oil. Its effect in the case of the paraffin wax ester tends to show that the acid-free ester and exclusion of acid formation by drying result in improved lubricating properties.†

Table 2 presents the results of the extension of the investigations to various oil-gas blends and straight polar compounds.

The values obtained for oil with gaseous additions, i.e., saturated with the gases, show an increase for oxygen and notably for carbon dioxide. The rise of the seizure load of oil on prolonged oxidation has been observed by King[6] and interpreted on the basis of the orientation theory. Hydrogen and carbon dioxide represent extreme cases of lowered and raised seizure points respectively, exactly as they show the frictional extremes in the experiments of Donandt. The greatest depression is, however, shown by oil + ammonia and by some other straight nitrogen compounds which may yield nitride on reacting with the iron, the formation of nitride with ammonia taking place at about 400° C. This case is of particular interest as the properties of the nitride, notably its hardness, may be demonstrated by changing the experimental conditions. On carefully running in the specimen with oil saturated with ammonia, the seizure point may be easily raised to about 1200 pounds. In this case the rough-ground steel surface is gradually polished due to its gradual surface hardening, whereas in the ordinary routine procedure few high spots are attacked and broken, resulting in a rougher, easily seizing surface with the exposure of fresh steel surfaces. In such cases, the most typical of which is presented by dixanthogene (sulfur), sometimes the whole surface of the test pin crumbles, thus wearing rapidly without any definite seizure point at all but very great friction.‡

In the case of highly active agents like ammonia and sulfur in its various compounds, strong effects of the concentration of the agent or of temperature should be expected which, in that case, amounts to the same, a certain rise of temperature being required for inducing the reaction locally and the rest of the liquid rather acting as a coolant. The effect of sulfur in a mineral oil, as shown in the table, should be interpreted in the same way.

From the effect of carbon dioxide and its interpretation as a chemical contamination of the rubbing surfaces, there is but a step to the interpretation of the effect of the esters as a "carbon dioxide" effect. More chemical investigations will be required to prove it directly as Schottky and Hiltenkamp proved it for nitration. What we can tell for certain is that all results indicate that we are neither dealing with phenomena of viscosity nor surface orientation or protective gas films.

According to the "oiliness" hypothesis based on surface orientation and boundary friction, briefly: strong adhesion and long chains as requisites, independency of effect on concentration, we should expect:

1. Approximately same seizure point for the ester blend and the straight ester—the experimental values are 900 and over 2500 pounds respectively.

2. Rather better than poorer performance of an acid compared with its ester. The experiments do show a very marked difference, however with the opposite sign.

3. Lowering of seizure point by carbon dioxide (short chain) and raise by stearonitrile (long chain). Both compounds will certainly be preferentially adsorbed by the metal, the former due to its large partial electric C=O moment[7] of about 1.8 D., the latter due to its extraordinarily large moment of about 3.4 D., a moment which is by no means hidden in the molecule. The experiment yields for both compounds about the same seizure value. A comparison between stearonitrile and long-chain esters is particularly illustrative because of the vastly larger dipole moment (adhesive force) of its active group. The much less adhesive esters of comparable chain type and length have up to twice the seizure value of the nitrile. This case is conclusive proof

*A discussion of these phenomena with photographs and a very complete bibliography is presented by G. Schmaltz in his excellent book "Technische Oberflachenkunde" (Technology of Solid Surfaces), Berlin 1936, pp. 212-215.

†These experiments and considerations have no connection with the well known experiments of E. G. Gilson, Ind. and Engin. Chem. **18**, 467, 1926, which still appear unexplained. We recall that Gilson's experiments on a modified Couette apparatus were made under conditions of strictly fluid lubrication.

‡When this part of the investigation was already finished two papers came to the author's attention: A. Fogg and C. Jakeman (Genl. Discuss. on Lubrication, Inst. of Mechan. Eng. London 1937, **1**, 465 and H. W. Brownsdon, loc. cit. **2**, 254.—The former paper deals with the effect of water in straight mineral oil, the latter with the influence of addition agents, including gases. Brownsdon's paper is a depart from the conventional treatment of the subject by his taking into consideration chemical reactions at the seat of friction in some cases, incidentally, not in the case of gaseous additions.

that neither adhesion nor chain length are the determining factors in the "oiliness" phenomena of practice.

The same considerations apply to viscosity or gas film effects, leaving for an explanation of the main effect the presence (vapor pressure!) and the individual mechanism of reaction of the lubricant with the surface.* A simple, well understood physical effect which happens to go parallel with the "degree of polarity" of any polar addition—exactly as adhesion does approximately—but for altogether different reasons, has been discussed in the preceding paper.

The occurrence of unexpected high-temperature reactions may be finally demonstrated by the effect of an addition of 1 percent carbon tetrachloride to oleic acid (commercial). The seizure point for the acid (1800 pounds) dropped by that addition to 1400 pounds, clearly showing that other reactions interfered with the otherwise so powerful extreme pressure action of the chlorine compound.

Temperatures in the range required to induce reactions between lubricant and surface have been measured by F. P. Bowden and K. E. W. Ridler.[8] Under conditions of boundary lubrication occurring in practice, the temperature may easily rise to 500° C. and higher, the actual bearing surface being very small and rather formed by point contacts where the pressure rises to very high values. These conditions are not limited to those cases where, in practice, extreme pressure lubricants are used. Boundary lubrication and kinetic friction of practice are always connected with wear, ensuing in a continuous breakdown and repair of the lubricating film as found by Bowden and his co-workers. The same phenomenon was observed in the operation of the author's friction pendulum.[9] This fact should be emphasized in order to exclude the misconception that these investigations are dealing with phenomena, occurring exclusively under conventionally so-called extreme-pressure conditions. They are common to all operating conditions which give rise to non-fluid lubrication and are moreover the basis for a correct understanding of the running properties of bearing materials, a subject which is being dealt with elsewhere.[10]

The phenomena of wear and seizure are illustrated by comparison with the analogous processes of soldering and welding. Both processes presuppose clean surfaces. In the case of non-fluid lubrication straight oils clean the surfaces by decomposing into unsaturated hydrocarbons and hydrogen. Seizure points differ little and are determined by the cracking characteristics of the oil—reasonably low volatility provided. Lubricants containing other elements (e.g. esters, amines), the majority of which is polar for that very reason, contaminate the surfaces by chemical reaction. As a matter of course, even a small amount of addition may be beneficial and adequate due to selective adsorption in cases where seizure is imminent on very few peaks only, i.e., when only very little contaminating agent is needed to prevent seizure. The resulting compounds have higher melting points than the metals and, thus, will less easily weld or interdiffuse. In some cases their physical properties may result in disintegration of the surface. Table 3 represents some characteristic data.

TABLE 3
Metals, Compounds and Melting Points

Metal		Compounds			
Al.....	658° C.	Al_2O_3	2020°	Al_2S_3	1100° C.
Pb.....	327° C.	PbO	879°	PbS	1112° C.
Cd.....	321° C.	.....	.....	CdS	> 1000° C.
Fe.....	1401° C.	Fe_2O_3	1565°	FeS	1197° C.
Cu.....	1084° C.	Cu_2O ca. 1230°	CuO 1148°	Cu_2S	1130° C.
Sn.....	232° C.	SnO_2 1127°	.....	SnS	880° C.

Measurements with the friction pendulum[9] permit a clean demonstration and separation of viscosity phenomena and show that they are still present at extremely small film thicknesses. This leads to the conclusion that most measurements of non-fluid friction yield, as a matter of fact, mixed coefficients of non-fluid friction and that in those cases where viscosity is really absent we are measuring rather the (still ill defined) dry friction of chemically-contaminated surfaces.

In a subsequent paper torque-pressure curves and the coefficient of "dry" friction shall be briefly discussed and some additional microscopic material on high-temperature reactions presented.

The author wishes to acknowledge a research fund provided during the years 1937 and 1938 by Union Oil Company of California and the cooperation and some special research facilities of the Research Department of that company through Dr. C. D. Barnes.

*It is evident that the original condition of a chemically changed surface cannot be restored by treatment with oil solvents, i.e., the running properties of a bearing may sometimes markedly depend on its history, e.g., on the oil which has been used for running in, as observed in practice (see D. R. Pye, The Internal Combustion Engine, vol. II., Oxford 1934, p. 102 et seq.). Attempting to account for that phenomenon by properties of adsorbed films, however, means ascribing to such films properties otherwise foreign to them; it is not an explanation but a postulate.

REFERENCES

[1]S. Kyropoulos, Refiner and Nat. Gas. Man., Vol. **18**, No. 7, p. 273.
[2]R. Holm and B. Kirschstein, Wiss. Veroeffentl. Siemens-Werke, **15**, (1.) 122. Berlin 1936.
[3]H. Donandt, Zeitschr. Ver. Deutsch. Ing. **80**, 823, 1936.
[4]M. Fink and U. Hofmann, Zeitschr. Metallkunde, **24**, 49, 1932, and Zeitschr. Ver. Deutsch. Ing. **77**, 978, 1933.
[5]H. Schottky and H. Hiltenkamp, Stahl u. Eisen, **56**, 444, 1936.
[6]R. O. King, Proc. Roy. Soc. Lond. **A, 139,** 447, 1933 and J. Inst. Petrol. Techn. **20**, 97, 1934.
[7]F. V. Lenel, Zeitschr. Physik. Chem. **B, 23,** 379, 1931.
[8]F. P. Bowden and K. E. W. Ridler, Proc. Roy. Soc. Lond. **A. 154,** 640, 1936. Abstract see: Genl. Discuss. on Lubr. Inst. Mech. Eng. London, **2**, 236, 1937.
[9]S. Kyropoulos and E. I. Shobert, Rev. Scient. Instr., **8**, 151, 1937.
[10]S. Kyropoulos, In press.

Helium . . .

Its Sources, Production and Use

A. W. TRUSTY

THE United States owns practically all of the world's supply of helium. Helium was discovered in the atmosphere of the sun by means of the spectroscope by Lockyer in 1868. Later, Ramsay detected it in the elements of the earth about 1895.

In the early days of the World War, the belligerents tried hard to find a gas to fill airships which would be light and non-inflammable. The first German Zeppelin brought down in England was ablaze when it fell over London after being struck by the fiery bullet from an airplane gun. The fact that they were filled with the highly-inflammable hydrogen gas was the greatest drawback to the success of the Zeppelins. The Allies turned to helium, which was known to be non-inflammable, but which was very expensive to produce. Secret plants were built and the commercial production of helium was attempted. So far had the work progressed that at the time the Armistice was signed in November, 1918, a consignment of 150,000 cubic feet of helium was on the dock at New York ready for shipment to France.

Helium is colorless, odorless, and tasteless. It is the most difficult of all the gases to liquefy. Like nitrogen and argon, helium has no chemical activity. With the exception of hydrogen, helium is the lightest element. A comparison of the properties of hydrogen and helium is shown:

	Helium	Hydrogen
Boiling point	—451°F.	—423°F.
Freezing point	—456°F.	—434°F.
Specific heat B.t.u./lb.	2.25 (—292°F)	4.75(—274°F)
Specific gravity (Air=1)	.138	.0695
Explosive limits	non-inflammable	6-71%

Hydrogen has a small advantage over helium in buoyancy. In air at normal atmospheric pressure and 60°F., 1000 cubic feet of pure helium will lift 65.82 pounds; 1000 cubic feet of pure hydrogen will lift 71.04 pounds.

Helium diffuses generally about three times as quickly as nitrogen (two-thirds as quickly as hydrogen). There are certain materials, for instance gelatine, celluloid, cellophane and ordinary glass at higher temperatures which are practically airtight but nevertheless possess an abnormally high permeability for helium.

An advantage that helium has over hydrogen is that helium can be purified. It is well known that during the operation of an airship some of the lifting gas escapes by diffusion through the walls of the cells, but perhaps it is not so generally known that the lifting gas, whether it is helium or hydrogen, becomes contaminated with air, which diffuses into the gas cells. In the case of helium the only effect is a reduction of the lift of the ship. With hydrogen, such dilution not only reduces the lift, but increases the hazard of fire and explosion. The mixture of helium and air can be taken from the ship and purified by a process similar to that used in extracting it from the natural gas. The helium is usually withdrawn from the airship for purification when the air content reaches about 15 percent by volume. About 6,000,000 cubic feet of helium is required to fill a ship of the size of the late Hindenburg.

Small quantities of helium are frequently wanted in scientific laboratories for various physical or chemical operations. On account of its inertness and high heat conductivity, it is valuable for cooling electric motors and fire-proofing high-tension switchboxes. It is also used for the filling of radio tubes, gas thermometers, etc. Helium gives a pale yellow light when used in electric signs. In deep-sea diving, helium is added to the oxygen atmosphere supplied to the diver. Helium is less soluble than nitrogen in the blood and escapes more quickly and in smaller bubbles as soon as the pressure is released; thus the so-called caisson illness can be avoided, and the decompression period shortened. In fact, this use of helium has resulted in much deeper diving than was heretofore possible with the use of oxygen and nitrogen.

Helium is found in the atmosphere in the proportion of 4 volumes of the gas to 1,000,000 volumes of air. It is a product of radioactive disintegration in all minerals and rocks containing uranium or thorium. It has been estimated that between 280 and 1050 million cubic feet of helium are generated annually by radioactive processes.

There are several places on the earth where the escape of helium, together with other gases, is especially marked. Here the quantities of helium which leave the earth's crust are so considerable that they cannot have been freshly formed from rocks by radioactive processes; they consist of "fossil" helium which has been collected during geological periods and has only recently found an opportunity to escape. Obviously, these sources of helium are not

constant in production and will come to an end after a definite period.

High concentrations of helium have been found in three groups of natural gases: gases from mineral wells, volcanic gases and petroleum gases. Each of these gases, however, may occur practically free from helium. Most of the helium-bearing gases from mineral wells in Italy, Germany and France consist almost exclusively of nitrogen; some of French origin also contain carbon dioxide in considerable quantity. In petroleum gases much nitrogen is an indication of the presence of helium; however, there is no proportionality between the helium and nitrogen content.

Although the percentage of helium is high in some of the gases in Japan, Italy and France, the total output of gas is small. It is improbable that industrial exploitation can be carried out on this type of gas.

Gases containing more than 1 percent of helium (which is generally considered as the lower limit for economical extraction) are uncommon even in the United States. The most important of the United States fields are the property of the government. While the Cliffside Field (Potter County, Texas), is exclusively used at present for drawing all helium necessary for the government, others are retained where the helium is stored in its natural reservoir underground. An estimate of the known helium reserves is shown:

	Cubic Feet
Eastern Rocky Mountain District:	
Southeastern Colorado	88,000,000
Northeastern New Mexico	8,000,000
Northwestern Texas	1,180,000,000
Western Rocky Mountain District:	
Southwestern Wyoming	2,399,000,000
Utah	216,000,000
Central District:	
Kansas	2,037,000,000
Grand Total	5,928,000,000

The quantity of helium present in the various gases is shown in Table 1.

Helium can be made from the air, but the cost is high. A British firm supplies helium made from air for $7.00 per liter. Helium also can be prepared in small quantities from radioactive minerals; but this method of course is limited in scope, and the price of the product is high.

The method of manufacturing helium at the government plant in Amarillo, Texas, is as follows: The gas is received under a pressure of 600 pounds and is first passed through a solution of caustic soda for the removal of carbon dioxide. The gas is then cooled to —300°F., which causes 95 percent of the gas to become liquid. The final stage is to subject that part of the original natural gas which is still in the gaseous state to a pressure of 2000 pounds and cool with liquid nitrogen. Since helium is the most difficult of all of the constituents of the natural gas to liquefy, this process of continual compression and cooling removes most of the hydrocarbons and other gases by liquefaction. The finished helium is 98 percent pure.

TABLE 1

Helium Gas in the United States

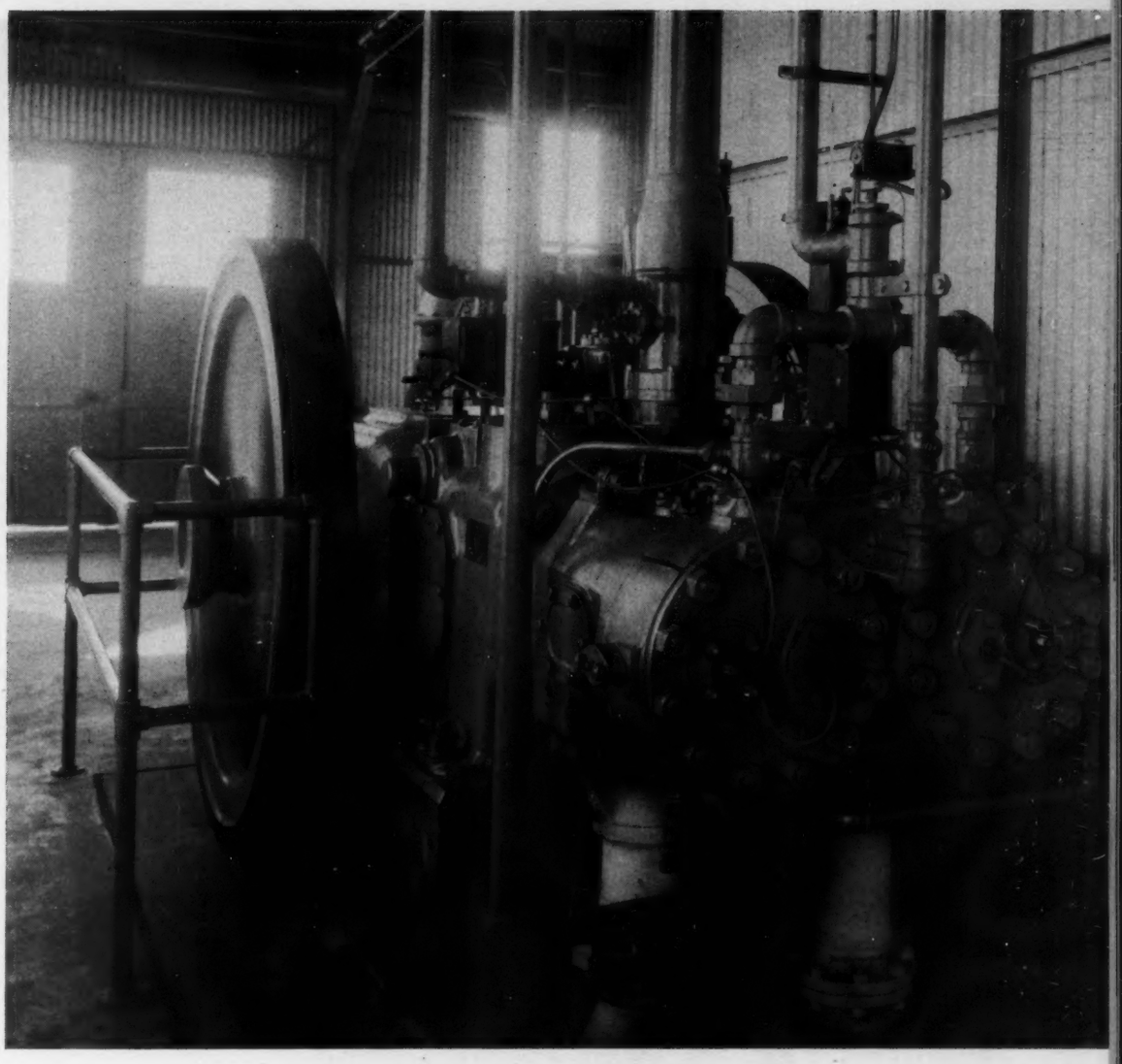
STATE	COUNTY	Methane and Ethane Percent	Nitrogen Percent	Helium Percent
Arkansas	Union	75	20	.04
Arkansas	Ouachita	95	4.49	.01
California	Los Angeles	99.5	.45	.02
Colorado	Las Animas	....	74..5	8.64
Colorado	Yuma	96.1	3.62	.07
Illinois	Crawford	84.85	3.70	.11
Kansas	Cowley	23.58	74.26	1.98
Kansas	Reno	51.79	46.75	1.04
Kentucky	Russell	98.4	.63	.36
Louisiana	Richland	82.0	17.76	.09
Louisiana	Caddo	....	....	.03
Louisiana	De Soto	....	....	.001
Mississippi	Hinds	99	.21	.001
Montana	Musselshell	....	54.0	16.00
New Mexico	Eddy	30.79	68.67	.04
New York	Allegany	99.50	....	.30
Oklahoma	Jefferson	62.20	36.59	.97
Pennsylvania	....	....	....	.08
Tennessee	Warren	99.0	....	.20
Texas	Potter	....	....	1.70
Texas	Eastland	97.75	.51	.04
Utah	Grand	17.0	1.0	7.07
Wyoming	Sweetwater	45.75	46.0	.89
Wyoming	Sweetwater	97.50	1.27	....

Italy and Canada have made attempts to produce commercial helium, but these plants have been abandoned. Private companies at Dexter, Kansas, and Thatcher, Colorado, since 1921 intermittently have produced helium for sale. The first government plant was located near Fort Worth, Texas. Later a plant was built at Petrolia, but both of these plants have been abandoned and at present the only government plant is located near Amarillo. It is estimated that the reserve supply of gas for the Amarillo plant is 100,000,000,000 cubic feet with a recoverable helium content of about 1.8 percent.

The Amarillo plant produced in the six years prior to 1935 more than 60,000,000 cubic feet of helium of 98 percent purity. The cost of the helium has been reduced from $34 per 1000 cubic feet to a gross cost of $8.20. Allowing for returns from the sale of the residue gas, the net cost of production is about $6.00 per 1000 cubic feet.

REFERENCES

The Science of Petroleum, Dunstan. Pages 1511-23.
International Critical Tables.
Stewart, U. S. Bureau of Mines Circular 6745. (1933).



The 125-horsepower gas engine is controlled with a diaphragm lever motor which governs operation of the light oil pump.

Modernized Cracking Plant Has Novel Features

J. C. ALBRIGHT

BARNSDALL Refining Corporation recently reconditioned its cracking plant at Barnsdall, Oklahoma, to make it modern in every respect, and to improve quantity and quality of products. The revamped unit has a capacity of 2700 barrels of charging stock per day, processing both light and heavy oil, employing two hot-oil pumps, each driven by a separate gas engine.

The flow of processed stock through the plant was not changed materially, except in those cases where it was to the advantage of temperatures, pressures and the resulting products to make revisions.

One of the major changes in the plant was in the selection and setting of the hot-oil pumps and their respective prime movers. Two gas engines were installed, each to operate independently of the other, but both to be equipped with automatic controlling devices so that a constant flow of stock might be pumped through the furnaces by instrument control of engine speed, regardless of temperature or pressure conditions in the furnaces, transfer lines of subsequent columns and equipment, obviously, of course,

Note diaphragm lever motor unit at right rear of engine mounted on the governor case of the 400 horsepower machine. This device controls speed of the engine to compensate for possible fluctuating flows of charging stock.

within the limits of reasonable operation procedure.

A new all-steel building was erected near the processing furnaces in which the engines were housed, partitioned with a dividing fire-wall, on the opposite side of which two reciprocating, outside plunger-packed hot-oil pumps were installed. One of these engines is a vertical, eight-cylinder, four-cycle unit which may be converted to Diesel with the necessary replacement of parts, and the other is a twin-cylinder, horizontal, two-cycle engine. The latter engine is connected through flexible couplings to the 4½- by 12-inch pump which handles approximately 192 barrels of stock per hour. The eight-cylinder engine is similarly connected to a 4½- by 24-inch pump, which handles approximately 245 barrels per hour. Each engine is equipped with magneto ignition, the eight-cylinder unit having two magnetos and two sets of spark plugs to operate as dual ignition, and each engine has its individual oil-bath air cleaner.

In order to provide for a constant volume of charging stock to the cracking furnaces, disregarding the normal pressure drop through the tubes and transfer lines, instruments are installed on each engine to perform the functions ascribed to the original constant-speed governors. In the case of the horizontal, two-cycle engine, the instrument is attached to the throttle so that the equipment governor is locked out of service. However, the constant-speed governor is set at a point to obtain a higher speed than that governed by the automatic instrument, so that if the air supply should fail, or damage occur to the instrument, the governor will take charge of the engine and prevent excessive speed.

The vertical, eight-cylinder engine is equipped with a similar controlling instrument, but attached in such manner that it operates through the original governor at all times, resetting the latter to compensate for work required of the engine due to higher pressures within the cracking plant, or reducing the speed to control the amount of oil which the pump handles.

In drawing a comparison between a constant volume charge, and a constant speed charge, it is stated that, with the latter, gas pockets will generate in the suction line, preventing the full volume of the cylinder to be filled with oil. Again, packing may be slightly defective, or a number of causes may prevent the functioning of the pump to full capacity delivery, all of which is reflected all the way down to the gas recovery plant, and recorded as wavy lines on the

recording charts and observed in a product of varying quality. With the constant-volume operation, regardless of conditions, within reasonable limits, the quantity of oil which may have been decided as an optimum amount that may be processed, is constantly being delivered by the pumps and passed through the system. This is reflected in appearance of recorder charts. No matter where they may be located, each instrument is marking a straight line on the paper at all times. It is reflected again in the attitude of stillmen who are relieved of much of the worry of plant operation, when they are certain that the complete unit is functioning correctly. Again, the quality, and the quantity, of products do not fluctuate.

Flow of material through the plant begins, with the small hot-oil pump, at a designated draw-off section in the evaporator which consists of products having a gravity of 19.8° A.P.I. and a temperature of 705° F. The pump running at controlled speeds delivers a constant volume (determined at any time a new run is begun or changed during any operating period) of charging stock to the processing furnace at a pressure of 375 pounds, gauge, or at higher pressures near the completion of a run when slight coking on the interior of the coils produces a higher drop in pressure.

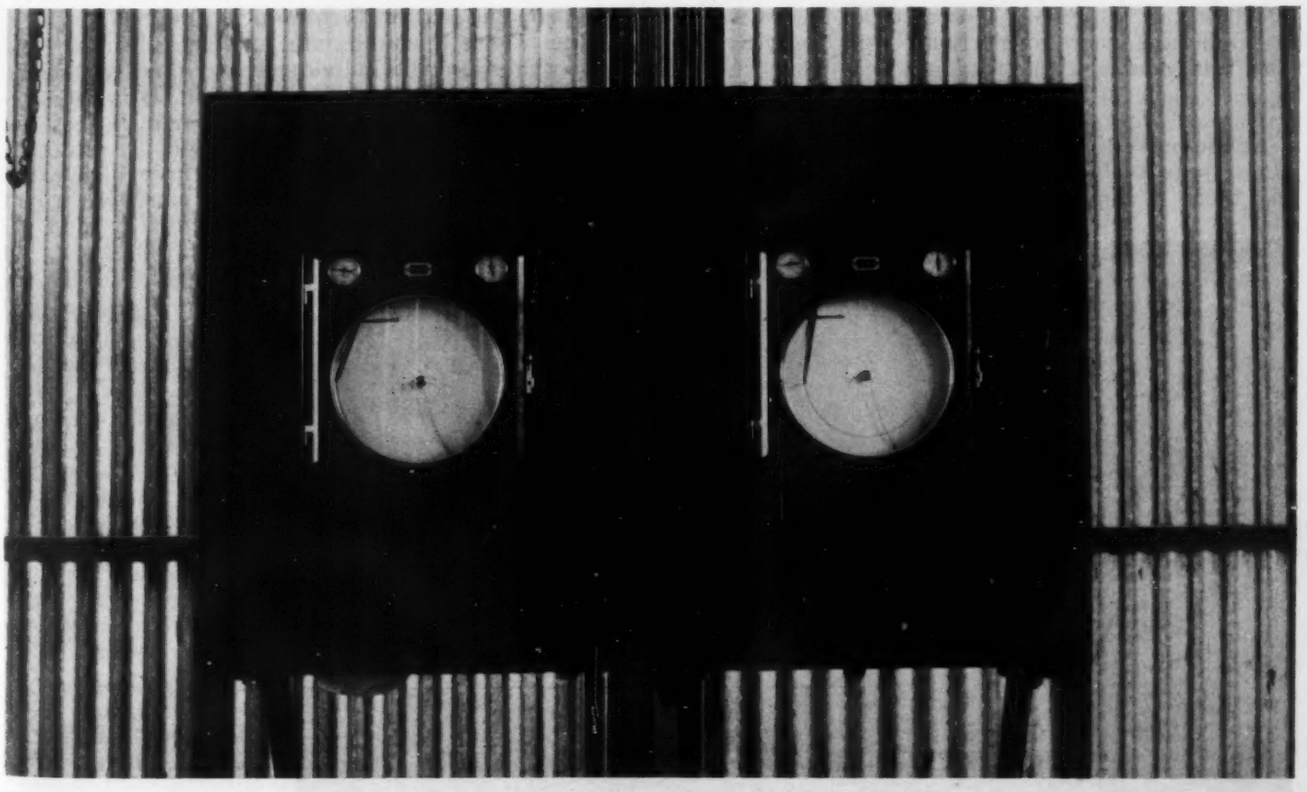
The material handled by the larger pump is taken from the base of the bubble tower at a temperature of 560° F., and delivered at the coils at a pressure of 1250 pounds, which increases slightly as coke begins to be deposited within the tubes. The pressure on the discharge line of this pump is that encountered at the beginning of a run, but the volume remains constant through the many days that the plant is on stream.

The discharge lines from both pumps are attached to roof girders, and extended below the eaves outside the pump-room building, and each is equipped with orifice flanges for instrument control of volume. The recording and governor-actuating instruments are in the building. The piping carrying the fluid from the orifice flanges down to the control instruments are laid beside live steam lines to prevent congealing of the material, and both pipes being covered with insulation to prevent radiation.

At the end of each run, both engines are given a thorough inspection, including cleaning of the various controlling instruments. All magnetos are removed and taken to the refinery machine and repair shop where they are completely overhauled, new parts replacing those found out of order and points ground and breaker gaps adjusted to the proper spacing, and new spark plugs installed. It is said that the difference between the price of a dozen and a half of plugs and a failure of engines is not enough to justify taking a chance on an emergency shutdown.

The plant is operated with a minimum of difficulty and temperature fluctuations since the installation of these volume-controlling instruments, particularly when a comparison is made between the present method of operating and that used before the plant was modernized. After the unit has been brought on stream and operating pressures and temperatures have been stabilized, all corollary instruments show a marked improvement in recording the process; furnace temperatures, fuel delivery, transfer temperatures, all have been straightened out on the recording charts.

The amount of work required to overhaul the instruments and place the ignition apparatus in good condition, together with material used, will not exceed $50.00 at the end of each run, practically all for labor, as frequently all material which may be required is a set of spark plugs.



Recorder controllers which control the speed of the gas engines driving charging pumps to secure a constant rate of flow.

ECONOMICS OF
Catalytic Polymerization of Natural Butanes

F. B. MACK
Shamrock Oil & Gas Corporation

Presented before the annual meeting of the Natural Gasoline Association of America, Tulsa, May 3 to 5, 1939

DURING the past several years a great deal has been written about processes for converting light natural gasoline fractions into motor fuel. Most of the presentations in the past, however, have dealt in a technical manner with the method of conversion, and have generalized with respect to the effect of economic factors on the results to be expected from actual operation over a period of time.

Shamrock Oil & Gas Corporation has had 26 months' experience in the operation of a plant which employs a method for the cracking of and the catalytic polymerization of natural butanes producing a high-octane-blending-value motor fuel. This plant is operated in conjunction with a natural-gasoline plant and a refinery, both of which supply raw material to be processed. It is intended in this paper to present information obtained in the operation of this plant and also to show some of the uses for the products obtained as well as information which will give indications as to costs and values.

The octane value of butane makes it a desirable fraction to use in blending motor fuel, except that the use of butane as such for this purpose is limited to relatively small percentages because of its high vapor pressure. The polymerization process adopted by Shamrock Oil & Gas Corporation offers a way to utilize butane where formerly no opportunity existed. The advantages thus obtained must be weighed against the cost to justify the investment and the operation.

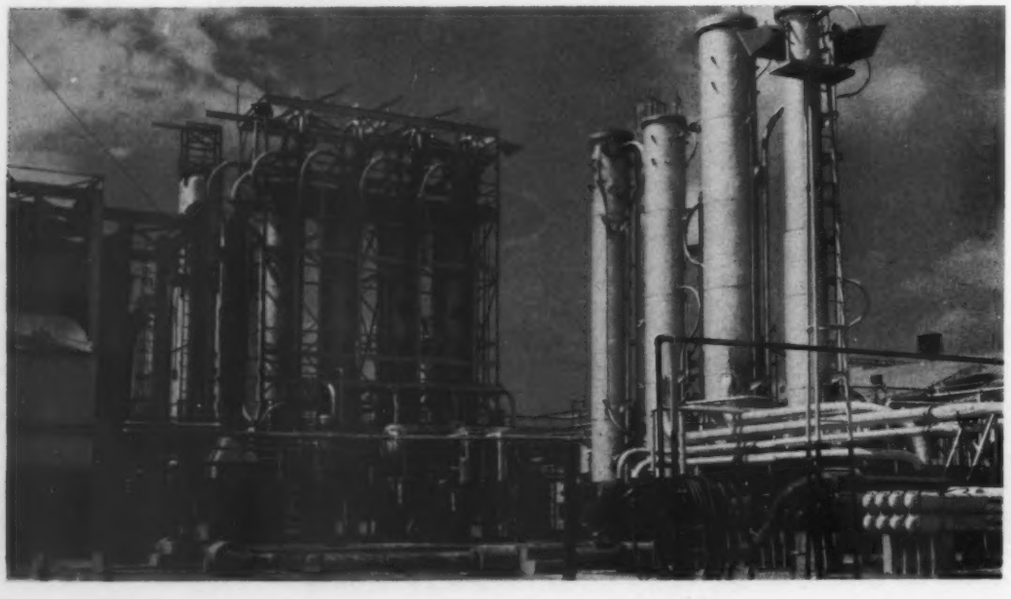
At the outset it may be stated that there can be no question as to the desirability of this product for use as a blend to improve the octane value of motor fuel. The cost of production, however, has been such that with low motor fuel prices the refinery demand has not developed in accordance with normal expectations.

The natural gasoline manufacturer who has quantities of excess butane sufficient for the consideration of this method of utilization should be able to reach a conclusion as to its advisability after giving the proper weight to the factors involved and the probable effect of those factors in the individual case. Generally speaking, the factors to be considered are as follows:

1. Quantities of butane available over a period of time.
2. Added investment to regular natural gasoline plant together with added costs of operation and maintenance.
3. Investment in polymerization plant and the cost of its operation and maintenance.
4. Probable market for products obtained.

When those questions are satisfactorily answered as they apply in the individual case, there should be no difficulty in reaching a conclusion. It is the purpose here to present neither an over-rating of the advantages nor to discourage those who are reluctant to take advantage of the opportunities which exist.

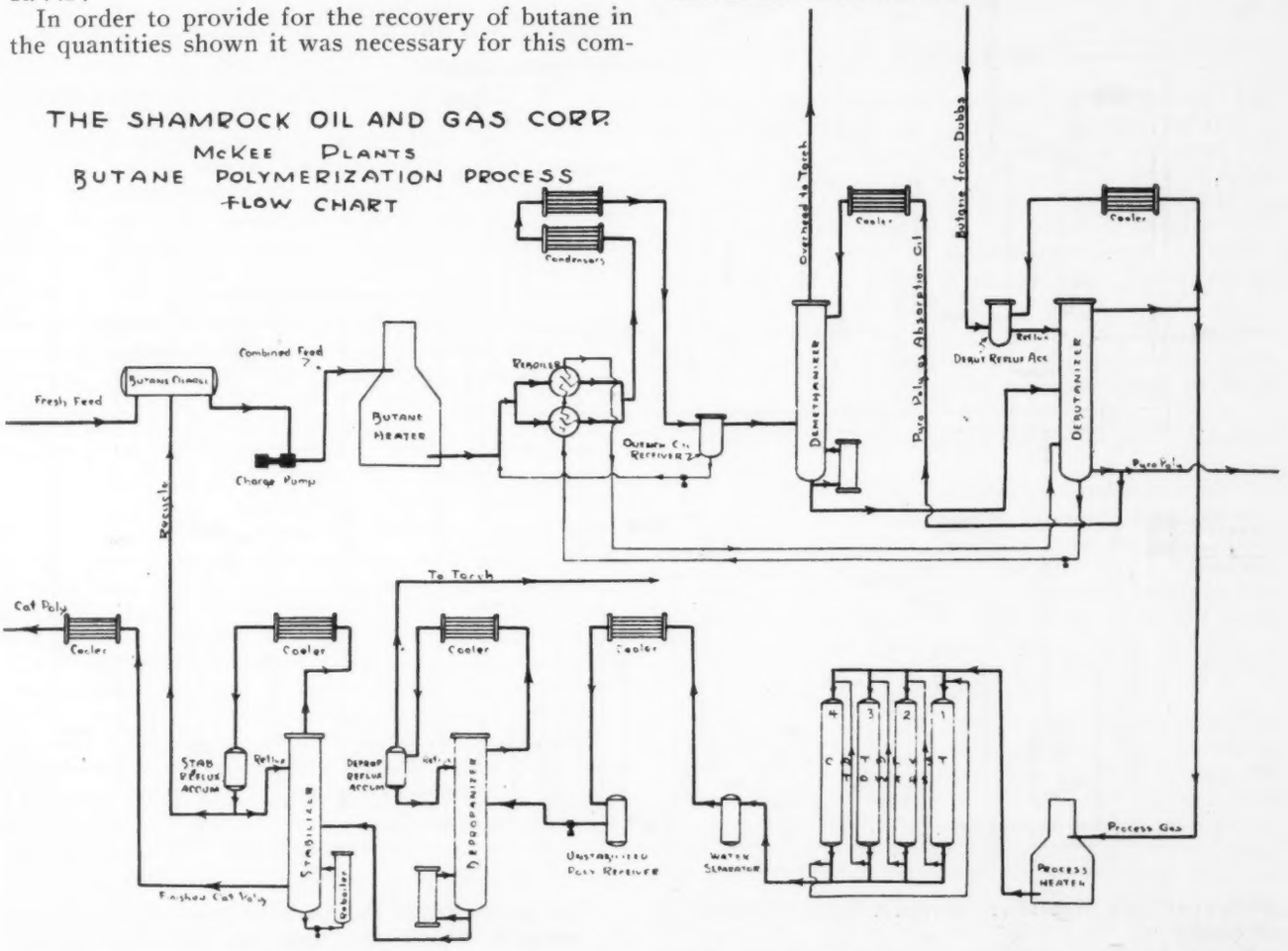
Shamrock Oil & Gas Corporation found that it had



General view of catalytic polymerization plant. Shamrock Oil & Gas Corporation, McKee, Texas.

available daily 600 barrels of butane at its McKee natural-gasoline plant in excess of that normally contained in 26-pound R.V.P. natural gasoline with 62 percent recovery of normal butane and 44 percent recovery of isobutane. This extraction is obtained with an absorber pressure of 240 pounds per square inch and an oil circulation rate of 8 gallons per 1000 cubic feet and with the use of a compressor plant to recompress the non-condensible vapors for additional butane recovery. It was found that this butane supply could be increased to approximately 1000 barrels per day if the vapor pressure of the natural gasoline manufactured were reduced from 26 to 18 pounds R.V.P.

In order to provide for the recovery of butane in the quantities shown it was necessary for this company first to increase its gasoline-plant equipment to provide for additional oil circulation, increased from a normal circulation of 4 gallons to 8 gallons per 1000 cubic feet of gas handled. This change necessitated increased heat-exchanger and preheater capacity as well as additions to the stills in order to strip the increased quantity of oil circulated. A primary still was installed between the heat exchangers and the preheaters to be operated at 65 pounds per square inch pressure and at an oil temperature of 250° F. The purpose of the increased oil circulation was to obtain a greater percentage of the lighter fractions which are normally not required in the manufacture of natural gasoline.



COMPRESSOR PLANT

All of these lighter fractions could not be condensed under the operating pressures and temperatures of the stills, and therefore, in order to effect the recovery of the butane desired, it was necessary to install a compressor plant to compress these uncondensed vapors to a pressure sufficient to recover the butane fractions. As an aid to recovering the butanes from the compressed vapors, the vapors were cooled to a temperature below that obtained with cooling water. This was accomplished by using the exhaust from an expander engine and expanding propane from the stabilizer to cool the compressed vapors in a chiller. This arrangement permitted a recovery of 92 percent of the butanes after extraction from the gas treated in the absorbers. The flow diagram of the natural-gasoline plant which is included with this paper shows the conventional natural gasoline plant with these added features.

The cost of the raw feed to the polymerization plant starts with the cost of the butane. To that must be added the cost, maintenance and operation of the additional equipment in the gasoline plant. It is not difficult in the individual case to arrive at this cost and apply the same on a unit basis to the cost of the finished product of the polymerization plant.

The cost of the polymerization plant when designed can be obtained on a quotation basis. The problem then becomes one of determining the cost of operation and maintenance of the polymerization plant and the recovery efficiencies which may be expected.

In addition to the cost of the polymerization plant and its operation and maintenance, the cost must include an allowance of one half of 1 cent per gallon for royalty and from one half to three fourths of 1 cent per gallon for the cost of catalyst.

The maintenance costs are subject to some con-

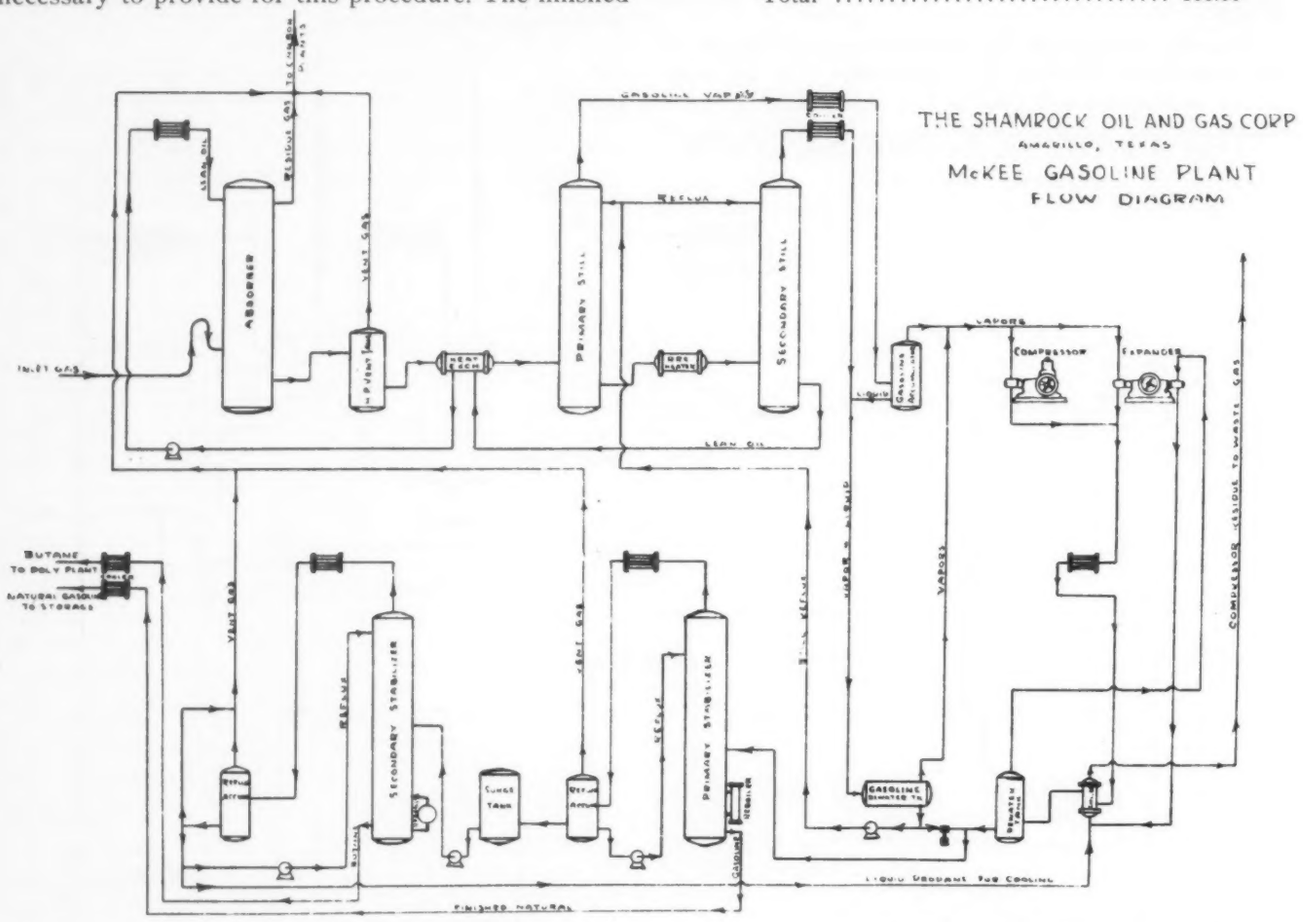
siderable variation. The plant has increased the length of runs between shutdowns from an average of about 15 to above 40 days. The cost of labor and material for shutdowns at first was $1600, but this cost has since been reduced to an average of $800 per shutdown. The plant can be operated with two to three men per tour.

To the costs considered thus far must be added the cost of rerunning, handling and treating. It was first thought that a rerun unit would not be required, but since difficulties were encountered with the end-point of the finished blends of motor fuel it was found necessary to provide for this procedure. The finished product is only slightly sour and a light treatment is necessary.

An analysis of furnace exit gases is given in Table 1.

TABLE 1

	Mol. %
Hydrogen	15.00
Methane	4.48
Ethylene	.05
Ethane	5.53
Propylene	11.36
Propane	15.17
Isobutylene	1.18
Butylene	.82
Butanes	46.00
Isopentane (plus)	.41
Total	100.00



In considering a plant such as this company has in operation, it should be kept in mind that the butane should contain a minimum amount of propane. The presence of propane in the feed has the effect of decreasing the capacity of the plant without compensation in yields. The utilization of propane for the production of polymers by the thermal cracking and polymerization method is receiving some attention at this time, however, and may ultimately offer possibilities. Since unit costs are vital to the profitable operation of a plant of this nature it follows that the rate of the charge must be maintained as high as possible.

DESCRIPTION OF PROCESS

The butane delivered to the polymerization plant is charged to a cracking furnace. The temperature and pressure of the furnace are controlled to permit the efficient production of olefins or unsaturates. The uncracked butanes are separated later in the process and returned to the charge tank to be recycled.

The gases from the furnace pass through heat exchangers which are used as reboilers for the debutanizer column. After the heat exchangers, the gases are condensed in atmospheric condensers and pass on through a quench-oil receiver into the demethanizer. A portion of the liquid is removed from the quench-oil receiver and reentered into the stream at the inlet of the exchangers as a control of the temperature of the liquid in the bottom of the debutanizer column.

The demethanizer column operates at 310 pounds pressure, with 150° F. bottom temperature and 90° F. top temperature. It is refluxed with an absorption oil for the purpose of making a separation between the ethane and lighter fractions and the propylene and heavier fractions. The bottoms of the demethanizer are fed into a debutanizer which operates at 275 pounds pressure, with 480° F. bottom and 200° F. top temperature. The pyrolytic polymer production, which is formed in the butane cracking furnace, is removed from the bottom of the debutanizer. A portion of this product is used as the absorption oil in

the demethanizer. The debutanizer is refluxed with the overhead product removed from the debutanizer in the refinery. The overhead from the debutanizer, consisting of butanes, butylene and propylene, passes through a process heater where it is heated to about 380° F. to 410° F. and then passes through the catalyst towers. The olefin content of the gas entering the catalyst towers averages about 24 percent. The catalyst towers are operated in series with three towers in use while a fourth tower is being reactivated. By rotation of the towers before reactivation the conversion efficiency is kept at a maximum. In this manner an average of 86 percent of the olefins entering the towers are polymerized. The vapors leaving the catalyst towers are condensed and then charged to the depropanizer. The depropanizer operates at about 310 pounds pressure, with 220° F. bottom and about 90° F. to 110° F. top temperature. There is some ethane in the feed to the depropanizer which was not removed in the demethanizer, so it is necessary to operate the depropanizer column at a high pressure to condense a sufficient amount of overhead product for reflux. The bottoms, which are essentially propane free, are fed directly into the stabilizer. The stabilizer operates at about 105 pounds pressure, with 360° F. bottom and 140° F. top temperature. The bottoms from the stabilizer are in the form of catalytic polymer, the vapor pressure of which is controlled between 6 pounds R.V.P. and 10 pounds R.V.P. as desired for blending. The overhead product of the stabilizer which is butane is condensed and returned to the charge tank to be recycled.

This plant was designed to operate with a combined feed of 2100 barrels and a fresh feed of 1100 barrels, which would give a ratio of combined feed to fresh feed of 1.91 to 1. It has been found in actual operation that a ratio of about 2.5 to 1 of combined feed to fresh feed results in a higher conversion of butane to polymer. Thus, by increasing the combined feed to 2500 barrels it was found that 1000 barrels of butane could be handled in this plant more efficiently, and that a conversion of butane to 10-pound R.V.P. polymer on a 40 percent yield basis could be obtained.

A flow diagram of the polymerization plant is included with this paper for use in connection with the description given.

In this process of cracking and catalytic polymerization of butane two products are obtained. The first product made is pyrolytic polymer, which is formed in the butane-cracking furnace and removed from the bottom of the debutanizer. The second product obtained is catalytic polymer, which is made by polymerizing the olefins in the catalyst towers. The production of pyrolytic polymer is about 8 to 10 percent of the total polymer production. Specifications of these two are in Table 2.

TABLE 2

	Before Rerun		After Rerun and Treated	
	Catalytic Polymer	Pyrolytic Polymer	Catalytic Polymer	Pyrolytic Polymer
Gravity, °A.P.I.	64	43.2	66.1	57.6
R.V.P.	6.1	5.8	7.4	5.5
Doctor	Positive	.....	Negative	Negative
Corrosion	Negative	.....	Negative	Negative
Color	Blue	.....	+26	+15
A.S.T.M. Gum	12.5 mgs.	.....	Nil	.5 mgs.
Oxygen bomb ind.	45 min.	15 min.	90 min.	60 min.
Sulfur, percent	.018	.02	.018	.02
Octane No. (L-3)	85.5	76	85.7	80.6
	(°F.)	(°F.)	(°F.)	(°F.)
I.B.P.	100	122	100	116
10 percent	150	168	142	158
20 percent	176	190	166	180
30 percent	191	206	188	195
40 percent	204	224	204	210
50 percent	220	247	220	226
60 percent	234	284	236	244
70 percent	260	345	256	270
80 percent	290	437	288	297
90 percent	338	492	326	324
E.P.	450	533	394	361
Recovery, percent	97	93	98	97
Residue, percent	1	1	1	1
Loss, percent	2	1	1	2

TABLE 3

	2nd Grade Motor Fuel		Special Blends	
	(1)	(2)	(3)	(4)
Straight run, percent	....	53	30	61.5
Catalytic polymer, percent	20	41	70	38.5
Pressure distillate, percent	70	...	....	....
18-pound natural, percent	10	6	....	....
Gravity, °A.P.I.	61.7	64.8	65.4	63.9
R.V.P., pounds	6.9	8.6	5.0	4.2
Gum, cu. dish, mgs.	....	....	2.6	2.7
Sulfur, percent	....	....	.04	.085
Octane No. (L-3)	72.9	72.4	83.0	74.5
I.B.P., °F.	98	97	....	....
10 percent, °F.	126	141	168	168
50 percent, °F.	225	226	214	213
90 percent, °F.	356	333	281	280
E.P., °F.	403	385	322	335
Recovery, percent	....	....	99.0	99.0
Residue, percent	....	....	.5	.5
Loss, percent	....	....	.5	.5

Table 3 gives the specifications of four blended products.

In the first blend, pressure distillate with an original 66-octane rating was blended with natural gasoline and catalytic polymer to produce a 72-octane fuel. The blending value of the catalytic polymer in this blend was 95. In the second blend, straight-run gasoline with a 50-octane rating was blended with catalytic polymer and natural gasoline to produce a 72-octane fuel. The blending value of the catalytic polymer in this instance was 102.

In Blends 3 and 4, a product was made which is comparable to some aviation fuels. The blending value of catalytic polymer in the third blend was 95 and in the fourth blend it was 98. The low gum in these special blends was obtained by the use of an inhibitor. The gum was determined by first subjecting the gasoline to an accelerated aging test at 212° F. with oxygen at 100 pounds pressure for four hours. Then 100 cc. of a mixture of the oxidized sample and gum solvent were evaporated and the residue reported as gum.

CONCLUSION

Polymer production is useful in blending special gasolines as well as regular motor fuel, and the possibilities of broader uses are still being explored. The greater percent has been used to blend the refinery gasoline to market specifications. The demand by other refineries has been limited as a result of the cost in comparison to low gasoline prices.

The desirable properties of polymer productions are (1) high octane blending value, (2) low percentage of sulfur, (3) low gum content, (4) high inhibitor susceptibility in blends of low end-point, and (5) distillation range of motor fuel requirements. The distillation range makes it possible to blend low grade gasolines to higher fuel specifications and the other properties make it possible to produce blends of higher market value.

Hydrogen Sulphide Removal

H. N. LaCROIX
and
L. J. COULTHURST
Design Engineers, Foster Wheeler Corporation

THE Tri-Potassium Phosphate Process may be summarized as follows:

The phosphate process for hydrogen sulphide removal has been proven both in efficiency and economy by experience gained from a number of commercial units in operation.

The phosphate process operates at minimum cost because the process is completely regenerative, the utility requirements are low, and substantially no replacement of chemical is required.

The phosphate process is a practical means for removal of H_2S from gases and permits operation at temperatures up to 200° F. For this reason, as well as the fact that the treating medium is an inorganic salt solution, condensation and absorption of valuable hydrocarbons is negligible.

The phosphate process is a completely regenerative method for hydrogen sulphide removal from liquid hydrocarbons in general.

The phosphate process requires only ordinary materials of construction; special alloys are not necessary; plant cost is low.

IT has long been recognized that hydrogen sulphide is undesirable in petroleum refining processes and the same objections exist in the chemical industry as a whole. Removal of the hydrogen sulphide is of the utmost importance to refiners and chemical manufacturers, as well as to consumers of the finished products. With the development of new methods for marketing and utilizing the lighter components of crude oils, the removal of H_2S assumes even greater importance to the refiner.

Among the detrimental effects are loss of product, reduction in process efficiency, and high maintenance costs due to corrosion of equipment. These apply particularly when hydrogen sulphide is present in charge stocks to polymerization plants, alkylation units, and in the production of iso-octane, hydrogen, aliphatic alcohols, various organic chemicals and liquefied propane and butane, also in natural gas, whether for domestic or industrial consumption. The hydrogen sulphide forms mercaptans, organic sulphides, and other sulphur compounds with the hydrocarbons, or deleterious reaction products with some catalysts or treating agents, in addition to having unpleasant odor and poisonous influence upon the human system. Sulphur compounds in the final products are difficult and expensive to remove by after treatment; consequently prior treatment of both liquids and gases is generally preferable. Even if the sulphur compounds are subsequently treated, the quality of the final product may be impaired, as for example, by reducing the octane rating or blending value of motor fuel.

Hydrogen sulphide may be removed by a number of methods and caustic soda wash is the simplest and probably the oldest. This method is effective, but for every pound of H_2S removed, 1.2 pounds of caustic soda is used. The soda is irretrievably lost and the cost of operating the process is high. H_2S may readily be removed, however, from gaseous or liquid hydrocarbons by means of an easy, regenerative process developed by Shell Development Company.* This process is based on the intimate contact with aqueous solutions of a simple, single compound, tri-potassium phosphate.

*U. S. Patent Numbers 1,945,163; 2,110,403; 2,157,879.

The tri-potassium phosphate method of H_2S removal acts in a manner similar to that of caustic soda since the solution acts as an alkali to hydrogen sulphide in absorbing it from its gas or liquid hydrocarbon carrier. The new process differs radically from the caustic-soda method, however, in that, after absorbing the H_2S, the solution will readily reverse its characteristics and expel the H_2S when heated to the boiling point. This permits the absorbing chemical to be reactivated continuously, thus restoring it to its original form and capacity for hydrogen-sulphide absorption.

FUNDAMENTALS OF THE PROCESS

The Tri-Potassium Phosphate Process for hydrogen sulphide removal from hydrocarbon gases and liquids is a continuous regenerative process based on absorption of H_2S to form compounds which may later be broken down by heating to a temperature slightly higher than the boiling point of water. Only cooling water and steam, or some other heating medium, are required for its operation beyond the initial charge of phosphate.

When treating large volumes of hydrocarbons having high hydrogen sulphide content, it is possible to recover the sulphur economically, either by conversion into elemental sulphur or sulphuric acid, or as hydrogen sulphide, essentially free of hydrocarbons or mercaptans. If the hydrogen sulphide has no value as such, it may be burned.

The absorption reaction is reversible and may be expressed as follows:

$$H_2S \text{ plus } K_3PO_4 \rightleftarrows KSH \text{ plus } K_2HPO_4$$

The direction of the reaction is controlled by temperature while the driving power of the reaction

depends upon the ratio of tri-potassium phosphate to potassium acid sulphide.

The treating medium (tri-potassium phosphate) is a stable inorganic salt solution having a specific gravity varying between 1.2 and 1.5. Basic ingredients for its manufacture are common caustic potash and phosphoric acid, both of average commercial purity and readily available at reasonable cost. They are used at a ratio of approximately three mols of KOH per mol of H_3PO_4. The solution is easily made and handled, and is not poisonous, volatile, corrosive or inflammable.

The concentration of the treating solution for use in this process depends on—

(1) The H_2S content of the liquid or gas to be treated.

(2) Desired purity of the product after treatment.

(3) Treating pressure.

(4) Treating temperature.

Gases have been handled with H_2S content as high as 3000 grains per 100 cubic feet and the gases after treatment contained as little as 15 grains per 100 cubic feet. Even lower H_2S content may be obtained if desired. Treatment may be at whatever pressure the gas or liquid is flowing. The use of tri-potassium phosphate permits treatment of gases at temperatures up to 200° F.—an appreciable advantage in preparing gases for polymerization.

A concentrated treating solution will retain more hydrogen sulphide per unit of volume than a dilute solution, but a dilute solution is capable of a more complete stripping from the fluid treated since it has a greater affinity for the H_2S. This characteristic is utilized to complete the stripping of the hydrocarbon gas just before it leaves the unit by contact with dilute treating solution after an initial contact with stronger solution. These solutions of K_3PO_4 normally range in concentration from 1.0 to 2.0 molal.

To illustrate the great affinity and capacity of tri-potassium phosphate-treating solution for hydrogen sulphide, a 31.8 percent by weight phosphate solution (about 1.5 molal) will contain over 3000 times as much H_2S as a mixture of liquid propane and butane in equilibrium with it, and after treatment, the propane-butane product at equilibrium contains only about 0.0006 percent by weight of H_2S.

Hydrogen sulphide may be satisfactorily removed from gases with tri-potassium phosphate over a wide temperature range up to 200° F. Furthermore, the treating medium has a negligible solution effect for hydrocarbons, since an aqueous inorganic salt solution is used. These characteristics of the process present distinct advantages in that, (1) entrainment of liquefied hydrocarbons with the treating solution may be prevented, and, (2) gas cooling requirements prior to treating may be reduced and possibly eliminated.

Control of the process is simple and plant operations may be made fully automatic, depending only on occasional specific gravity determinations of the phosphate solution, and Tutweiler or Orsat determinations of hydrogen sulphide in the outgoing product to obtain the desired control settings. Since it is only necessary to maintain the specific gravity of the phosphate solution, the operation of the process is independent of any special component ratios, acid-alkali balance or hydrogen ion concentration. There are no volatile components to pollute the purified gas or liquid products, and no deleterious side reactions take place.

Experience in plant operation has shown that there are no equipment corrosion problems. The materials of construction, therefore, are simple and inexpensive; cast iron and low carbon steel are used throughout and no special alloys are necessary. Standard heat exchanger and condenser practice is followed and either reciprocating or centrifugal

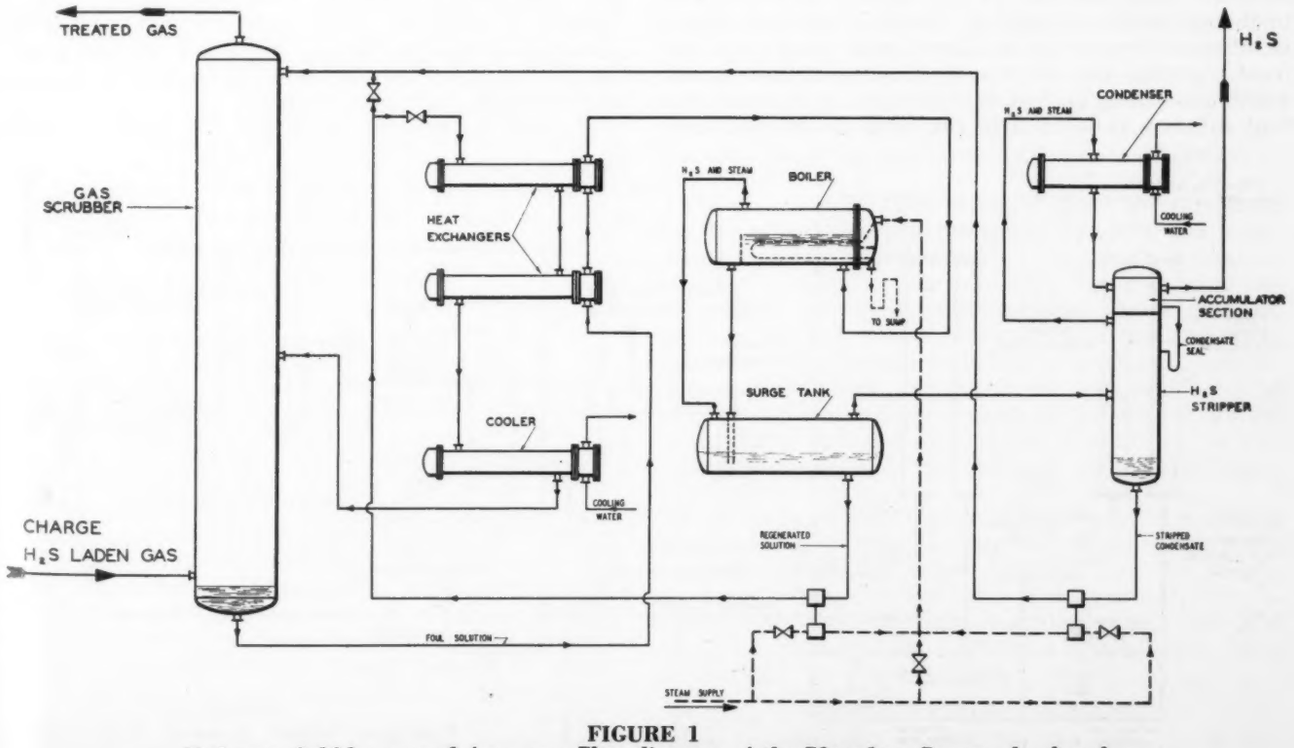


FIGURE 1

Hydrogen Sulfide removal from gas. Flow diagram of the Phosphate Process developed by Shell Development Company.

pumps may be used. Overall maintenance costs are practically negligible.

DESCRIPTION OF THE PROCESS

Diagrammatic flow sheets of the hydrogen sulphide removal processes, one for treating gases and the other for treating liquids, are shown in Figures 1 and 2 respectively, and described as follows:

In brief, gases bearing hydrogen sulphide are exposed to intimate contact in a scrubber tower first with a strong tri-potassium phosphate solution and then with a weak solution, in order to produce a treated gas that is relatively free of hydrogen sulphide. After absorbing H_2S, the foul solution is regenerated by boiling, which reverses the chemical reaction, dispels the H_2S, and restores the treating solution for recirculation. The heating evolves hydrogen sulphide vapor and evaporates water. These combined vapors are then separated in a stripper; hydrogen sulphide is vented at the top and water collected at the bottom. This water is returned to the top of the scrubber to be used again in making up the weak treating solution.

TREATING SECTION

In detail, gaseous charge stock containing hydrogen sulphide enters near the bottom of a scrubber, filled either with a system of bubble trays or with tower packing. As the gases rise, they receive a series of contacts with aqueous, tri-potassium phosphate solutions of two strengths, first, with a strong concentration having high capacity for H_2S, in the lower half of the tower, and then with a dilute solution, having high affinity for H_2S, in the upper portion of the tower. In this manner, the hydrogen sulphide content of the treated gas is reduced to a minimum before it leaves at the top of the scrubber, substantially free of hydrogen sulphide and ready for any further processing.

The weak tri-potassium phosphate solution, introduced at the top of the scrubber, flows downward through the upper half of the tower, countercurrent to the gas under treatment. Stronger solution, which is introduced near the middle of the tower joins the weak solution and the combined streams flow downward, absorbing H_2S at a rapid rate. A reservoir for foul solution is located in the base of the scrubber. All of the hydrogen sulphide extracted from the gas is contained in the foul solution, in the form of potassium acid sulphide, and the solution flows continuously to the regeneration section, generally under absorber pressure.

REGENERATION SECTION

Foul solution from the base of the gas scrubber is conducted through a series of heat exchangers in which the desired preheat is obtained from the hot regenerated treating solution, and is then ready to be regenerated. Regeneration is accomplished simply and quickly by holding the solution at the boiling point a short time until the reversal of the absorption reaction has taken place. A simple kettle-type reboiler is all that is required for this purpose. The boiling takes place normally at temperatures in the vicinity of 225 to 240° F., and, hence, exhaust steam from the pumps may be used as a source of heat. The chemical reaction is reversed and the solution restored to its original components, ready for recirculation. Hydrogen sulphide, saturated with steam, is evolved within the boiler, conducted to a surge tank, and ultimately piped into the hydrogen sulphide stripper. There remains a strong, regenerated solution of tri-potassium phosphate, concentrated in proportion to the amount of water boiled off.

At the rear of the boiler the regenerated treating solution spills over a weir into a sump from which it flows by gravity into the surge tank. The concentrated fresh treating solution is continuously withdrawn by means of a pump and most, or all, of it is passed through heat exchangers where its heat is used to preheat the cooler spent solution. This results in economy of cooling water and heating steam. The regenerated solution may be further cooled, if necessary, to the desired treating temperature in a shell-and-tube cooler, employing water as a cooling medium, and is then introduced directly at the midsection of the gas scrubber. A small portion of the hot regenerated solution from the surge tank is blended in a mixing valve with stripped condensate and introduced into the top section of the gas scrubber to maintain the desired concentration of weak tri-potassium phosphate solution.

In order to recover water for the dilute treating

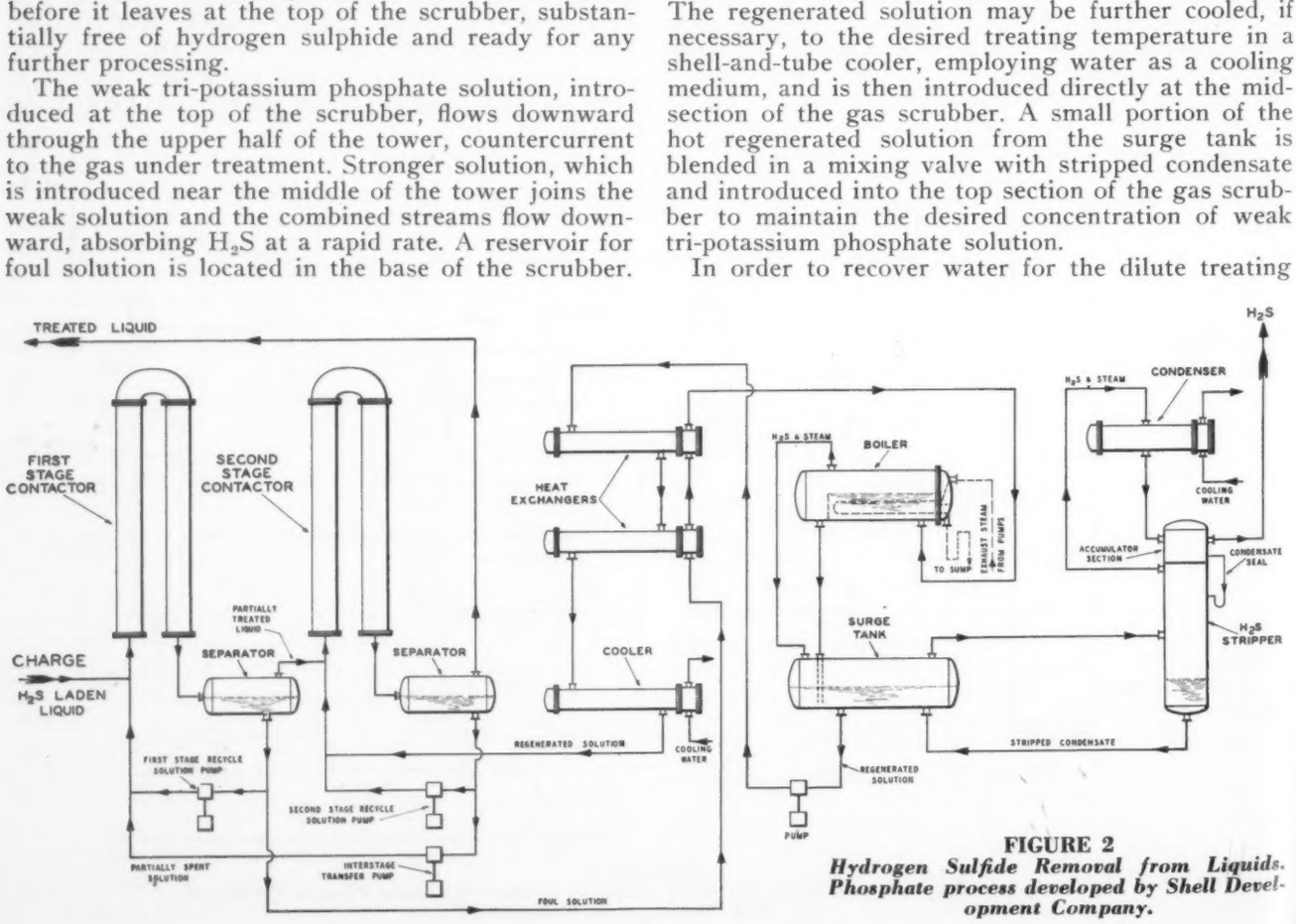
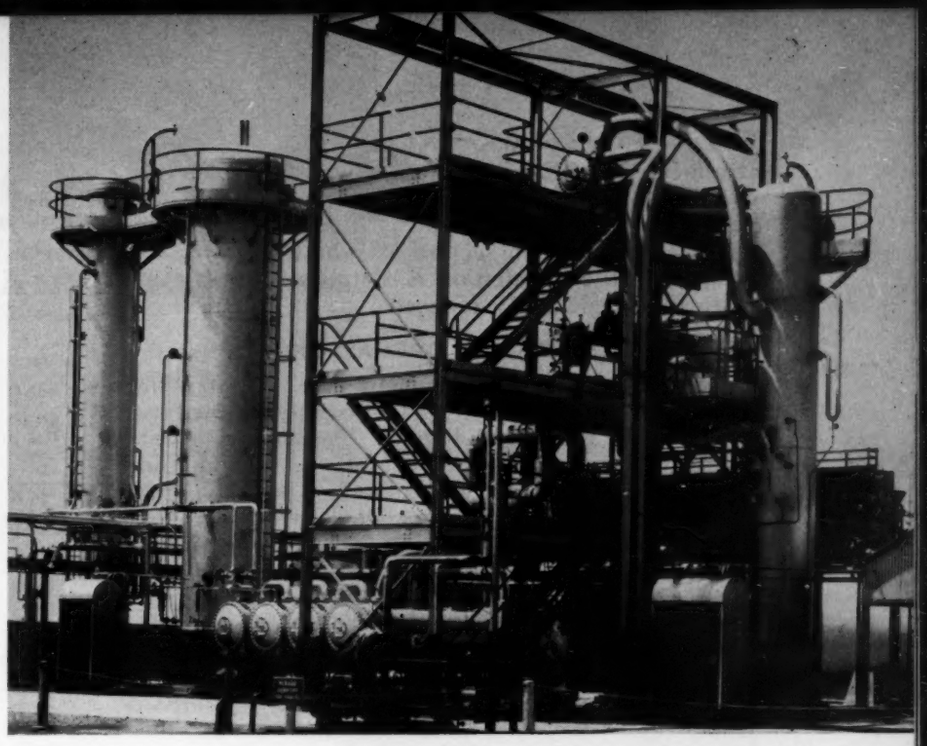


FIGURE 2
Hydrogen Sulfide Removal from Liquids. Phosphate process developed by Shell Development Company.



General view of large tri-potassium phosphate unit for simultaneous treatment of two refinery gases of different compositions, having a single regeneration section. The combined capacity of the two absorbers is 13,000,000 standard cubic feet per day and the H_2S is marketed for sulphuric acid manufacture. From left to right are the two absorbers, cooler and heat exchangers, surge tank, reboiler, condenser and stripper.

Photo Courtesy Shell Development Company

solution and to liberate hydrogen sulphide from the unit in a relatively dry state, it is necessary to separate the hydrogen sulphide from the steam that was evolved with it in the boiler. Steam and hydrogen sulphide from the surge tank are introduced to a stripper column just below a series of bubble trays filled with partially stripped condensate. As the vapors rise through the trays, part of the steam is condensed and the H_2S separated from this condensing steam. On leaving the stripper, the vapors flow to a shell-and-tube, water-cooled condenser where the steam is condensed. The H_2S gas returns with the condensate to an accumulator section at the top of the stripper where a temperature of about 90° F. is maintained. Here, the H_2S vapors are dried of nearly all of the water present since the vapor pressure of water is less than 37 mm. of mercury at 90° F. The H_2S is then readily vented from the system. The condensate is returned to the stripping section as reflux, flows downward over the bubble trays and is denuded of any remaining hydrogen sulphide. Stripped condensate is continuously removed from the bottom of the stripper and pumped to the top of the gas scrubber for blending with regenerated solution to form weak treating solution.

Hydrogen sulphide can be removed from liquids even more easily than from gases due to the fact that at the same temperature and pressure, the distribution factor for H_2S is three times more favorable for treating liquids than for gases. Moreover, a more favorable contact is possible in the liquid phase with the aqueous tri-potassium phosphate solution. Briefly, liquids bearing hydrogen sulphide are first treated with a partially spent tri-potassium phosphate solution in a mixer, then separated out, treated a second time with freshly regenerated solution, separated again, and withdrawn from the system essentially free of hydrogen sulphide.

TREATING SECTION

Aqueous solutions of tri-potassium phosphate and liquid hydrocarbons are immiscible and it is necessary, therefore, to obtain intimate contact between them in a mixing device. Two stages of vertical contactors are used for this purpose. The liquid charge stock containing hydrogen sulphide is joined by a partially-spent treating solution and the two liquids are then thoroughly intermixed in the first-stage contactor. From here they pass into a horizontal tank, identified as the first-stage phase separator, which operates full of liquid. Here, the heavier, foul treating solution is segregated as a lower layer. The upper layer of lighter, partially-treated liquid hydrocarbon leaves at the top of the tank and flows into the second-stage contactor, for treatment with fresh solution.

Freshly regenerated treating solution is introduced into the second contactor and the two liquids are again thoroughly intermixed just as in the first stage. They are then passed into the second-phase separator where the tri-potassium phosphate solution again separates out as the bottom layer. At the top of the separator the treated liquid, from which essentially all of the hydrogen sulphide has been removed, is finally collected and withdrawn continuously from the system.

The freshly-regenerated treating solution is introduced only at the inlet of the second contactor and after being used for the final treatment of the liquid, is separated out as partially-spent solution. Part of this solution may again be passed through the second stage by means of the second-stage recycle pump, if desired. Where H_2S is to be removed from liquids having high concentrations, no recycle is usually necessary since the volumetric ratio of phosphate to hydrocarbon is high enough to assure adequate contacting efficiency, but in many cases a certain amount of solution recirculation is advisable in each stage.

The remainder of the partially-spent solution from the second-stage separator is delivered by the interstage transfer pump to the first-stage contactor where it is joined by the incoming liquid bearing the full charge of hydrogen sulphide. After passing through the first-stage contactor, the treating solution is heavily charged with H_2S in the form of potassium acid sulphide. A portion of this foul solution may be recirculated by means of the first-stage recycle pump and the remainder is returned to the regeneration section for removal of the hydrogen sulphide.

Thus, only freshly regenerated tri-potassium phosphate solution is used for the final cleaning up of the liquid in the second-stage contactor, and the incoming liquid charge, laden with hydrogen sulphide, is treated only with partially-spent solution. The foul solution is returned for regeneration only after passing through both of the contact stages.

REGENERATION SECTION

The regeneration section for the removal of hydrogen sulphide from liquids is identical in general

arrangement with the corresponding section for the treatment of gases. In locations where hydrogen sulphide is to be removed from both gases and liquids, a single regeneration section may be used, with the result that the installation is simplified and the investment considerably reduced.

PLANTS IN OPERATION

A number of plants are using the Tri-Potassium Phosphate process to remove hydrogen sulphide from hydrocarbon gases and liquids. There are 5 plants together charging hydrocarbon gas at a combined rate in excess of 35,000,000 cubic feet per day. Individual units range in capacity from 2,000,000 to 13,000,000 cubic feet daily. The gases charged range from low hydrogen sulphide content to as high as 3000 grains per 100 cubic feet, and the treated gases contain as low as 15 grains per 100 cubic feet.

The liquid-phase process is now in commercial use in 2 plants for treating liquid propane and butane mixtures and may be applied to heavier hydrocarbons where the hydrogen sulphide content warrants such treatment.

The hydrogen sulphide gas that is separated out in these plants is burned as fuel or waste gas in most cases. In some instances the hydrogen sulphide is used for the manufacture of sulphuric acid as in one plant where the H_2S is separated at a pressure of approximately 15 pounds gauge with a purity of 99.3 percent and is delivered at its own pressure through a pipe line, ¾ mile long, to a neighboring chemical plant.

OPERATING COSTS

The water and steam requirements for plants removing hydrogen sulphide with Tri-Potassium Phosphate solution are shown in tabular form in Table 1. A limited amount of electricity is required for lighting and instruments, but this is negligible in comparison with the value of steam and water, as shown. Operating costs are low due to the efficiency of the phosphate as a medium of absorption, to the high degree of heat exchange, and to the fact that experience has demonstrated that there is substantially no loss of the chemical used for treating. In this process live steam may generally be used for all of the pumping services within the unit. The exhaust steam from these pumps is used again as a source of heat for the boiling and regeneration of the foul phosphate solution. The total steam requirements are further reduced by using heat exchangers to preheat the spent solution on its way to the regeneration system; cooling water requirements are likewise reduced. Although the treating solution consists mostly of water, the system is closed and loss of water is negligible.

Process handling losses may be neglected because the slight leakage of phosphate at stuffing boxes of pumps is readily collected and returned to the system. Heat for regenerating the spent solution may be furnished by a direct-fired boiler or by any other heating medium, and the pumps may be motor-driven, if desired.

TABLE 1

Example of water and steam requirements for 100 lb. hydrogen sulphide removal from gases of various contaminations

Based On: Treatment to final purity of 50 grains per 100 standard cubic feet.
Absorbing temperature—170 deg. F.
Pressure—200 lb. per sq. in. abs.
Equilibrium Solution Concentration—2.0 Molal K_3PO_4.

Inlet Gas Grains H_2S per 100 s.c.f.	500	1000	2000	3000
Percent H_2S Removal	90	95	97.5	98.3
Lb. Steam per 100 lb. H_2S Removed (Basis 50 lb./sq. in. ga. pressure)	1540	1010	860	780
Gal. Water per 100 lb. H_2S Removed (Basis 20° F. temperature rise)	7870	4920	4060	3600

PROCESS APPLICATION

The Tri-Potassium Phosphate Process for hydrogen sulphide removal has applications as follows:

1. Treatment of hydrocarbon and other gases to recover a treated gas with hydrogen sulphide content as low as 5 to 10 grains per 100 cubic feet.
2. Treatment of hydrocarbon liquids charged to polymerization or alkylation units where hydrogen sulphide is deleterious to the process.
3. Treatment of gasoline prior to mercaptan removal.
4. Recovery of hydrogen sulphide in concentrated form from gases and liquids for chemical use.

TABLE 2

Conversion Factors

Grains per Hundred Standard cu. ft. vs. Pounds per Million Standard cu. ft.

Grains/100 s.c.f.	100	200	300	400	500	600	700	800	900
Pounds/million s.c.f.	143	286	429	571	714	857	1000	1143	1286

Volume percent corresponding to grains per 100 standard cubic feet*

In Increments of 100 Grains per 100 Standard Cubic Feet		In Increments of 10 Grains per 100 Standard Cubic Feet									
Grains	**Percent**	**10**	**20**	**30**	**40**	**50**	**60**	**70**	**80**	**90**	**100**
.....	....	.016	.031	.047	.063	079	.094	.110	.126	.141	.157
100	.157	.173	.189	.204	.220	.236	.252	.267	.283	.299	.314
200	.314	.330	.346	.362	.377	.393	.409	.425	.440	.456	.472
300	.472	.487	.503	.519	.535	.550	.566	.582	.597	.613	.629
400	.629	.645	.660	.676	.692	.708	.723	.739	.755	.770	.786
500	.786	.802	.818	.833	.849	.865	.881	.896	.912	.928	.943
600	.943	.959	.975	.991	1.006	1.022	1.038	1.053	1.069	1.085	1.101
700	1.101	1.116	1.132	1.148	1.164	1.179	1.195	1.211	1.226	1.242	1.258
800	1.258	1.274	1.289	1.305	1.321	1.336	1.352	1.368	1.384	1.399	1.415
900	1.415	1.431	1.447	1.462	1.478	1.494	1.509	1.525	1.541	1.556	....

* 636 grains per hundred cubic feet equals one percent.
Note: Standard cubic foot measured at 60° F. and 760 mm. absolute pressure.